

1 Summary of things you should already know

“I think I can safely say that nobody understands quantum mechanics” Richard Feynman

1.0 Prerequisite

All material covered in Junior Honours Quantum Mechanics is part of the syllabus of this course.

1.1 Understanding Nature

Quantum Theory encompasses our best understanding of how nature works: what will be the result of any experiment. We arbitrarily split the universe into “system” (wavefunction), an environment or measurement (Hamiltonian, or operator) and a measurable quantity (eigenvalue). There is no unique associated mathematics, but since all measurements on systems yield real numbers, we need mathematics which gives real eigenvalues. So it is a premise of quantum theory that any measurable quantity is associated with a Hermitian operator.

1.2 Matrix and operator mechanics

There are two equivalent mathematical ways of calculating physical properties, Schroedinger’s wave mechanics and Heisenberg’s matrix mechanics. In each systems are represented in terms of eigenstates and measurables as eigenvalues. In matrix mechanics the operator is represented by a Hermitian matrix of elements $\langle m|\hat{Q}|n\rangle$ which depends on the choice of basis set $|m\rangle$. Any state can be represented by a normalised *vector*, which also depends on the basis set. The eigenvalues and eigenvectors of the matrix, however, do not depend on the choice of basis - the eigenvectors are, in fact, the eigenbasis of the operator.

For a set of basis ‘vectors’ of size N , there are $N \times N$ possible matrix elements.

1.3 Operators and Observables

In addition to position, a full description of a system must contain some implicit information. The abstract bra-ket notation includes this.

Consider the electric charge. Obviously this is measurable, so it should be associated with an operator \hat{Q} , such that e.g.

$$\hat{Q}|\Phi\rangle = -e|\Phi\rangle$$

where Φ is the wavefunction of an electron. $-e$ meets all the criteria for a quantum number, and the above equation is obviously a true representation of reality. Thus the meaning of the ket $|\Phi\rangle$ is broader than a simple spatial function, and operators can also be non-algebraic. This is especially important in particle physics where all manner of quantum numbers appear (isospin, strangeness, baryon number etc. etc.)

1.4 Changes in time

Schroedinger’s equation $\hat{H}\phi = i\hbar\partial\phi/\partial t$ shows us that the Hamiltonian (energy operator) is related to the change in wavefunction in time. A system prepared in an eigenstate of the Hamiltonian has time-invariant probability density. A system prepared in an eigenstate of a non-commuting operator has a probability density which varies in time. It is this time independence (conservation law) which makes eigenstates of the energy operator so useful.

When we measure some property of a system, the act of making the measurement collapses the system into an eigenstate of the appropriate operator. All memory of the previous state of the system is lost in this collapse, except in the special case when the state is degenerate, as we'll see later. The system then evolves according to its Hamiltonian.

1.5 Formal definition of a complete, orthonormal basis set

Consider a basis set $|i_n\rangle$. It is *orthonormal* if $\langle i_n | i_m \rangle = \delta_{mn}$. It is *complete* if any wavefunction can be written as $|\phi\rangle = \sum_n c_n |i_n\rangle$ and the c_n are uniquely defined. If the wavefunction cannot be so written, the basis set is *incomplete*, if there exists more than one possible set of c_n , the basis set is *overcomplete*. Choosing a basis set in a Hilbert space (see 1.7) is analogous to choosing a set of coordinates in a vector space. Note that completeness and orthonormality are well defined concepts for both vector spaces and function spaces.

1.6 Example of matrix representation method and choice of basis

In practical quantum problems, we almost always describe the state of the system in terms of some basis set. Consider a simple spin 1/2 system, choosing as basis states $S_z = \pm \frac{1}{2}$. Consider this system in a magnetic field pointing in the x direction, the operator corresponding to this is $\mu B \hat{S}_x$. We wish to find the eigenstates and eigenenergies.

Evaluating the required matrix elements such as $\langle S_z = \frac{1}{2} | \mu B \hat{S}_x | S_z = \frac{1}{2} \rangle$ (see QP3) gives a matrix:

$$\begin{pmatrix} 0 & \mu B/2 \\ \mu B/2 & 0 \end{pmatrix}$$

The normalised eigenvectors of this matrix are $(\sqrt{\frac{1}{2}}, \sqrt{\frac{1}{2}})$ and $(\sqrt{\frac{1}{2}}, -\sqrt{\frac{1}{2}})$ with eigenvalues $(\mu B/2)$ and $(-\mu B/2)$. Of course these represent the eigenstates $|S_x = \pm \frac{1}{2}\rangle$ in the basis of $|S_z = \pm \frac{1}{2}\rangle$:

$$|S_x = \pm \frac{1}{2}\rangle = [|S_z = \frac{1}{2}\rangle \pm |S_z = -\frac{1}{2}\rangle] / \sqrt{2}$$

Had we chosen $|S_y = \pm \frac{1}{2}\rangle$ as our basis set, then the matrix would have been:

$$\begin{pmatrix} 0 & -i\mu B/2 \\ i\mu B/2 & 0 \end{pmatrix}$$

Once again, the eigenvalues of this matrix are $(\mu B/2)$ and $(-\mu B/2)$, as they must be since these are the measurable quantities. Coincidentally, the eigenvectors in this basis set are also $(\sqrt{\frac{1}{2}}, \sqrt{\frac{1}{2}})$ and $(\sqrt{\frac{1}{2}}, -\sqrt{\frac{1}{2}})$.

Had we chosen $|S_x = \pm \frac{1}{2}\rangle$ as our basis set in the first place, the problem would have been much simplified. The matrix would then be:

$$\begin{pmatrix} \mu B/2 & 0 \\ 0 & -\mu B/2 \end{pmatrix}$$

Once again, the eigenvalues of this matrix are $(\mu B/2)$ and $(-\mu B/2)$, and now the eigenvectors are (1,0) and (0,1): i.e. the eigenstates are simply the basis states.

1.7 Dirac Notation - Analogies with vectors and matrices

You probably remember Dirac notation as a shorthand for integrals, for example the overlap between two wavefunctions can be written as:

$$\langle \chi | \phi \rangle \quad \text{instead of} \quad \int \int \int \chi^*(\mathbf{r}) \phi(\mathbf{r}) d^3\mathbf{r}.$$

(Where $d^3\mathbf{r}$ is the scalar volume element, sometimes called $r^2 \sin \theta d\theta d\phi dr$, $dx dy dz$, dV or $d\tau$)

But also if we have a complete set of orthonormal basis states i , the overlap is also the sum of the overlaps between each i and χ and ϕ

$$\langle \chi | \phi \rangle = \sum_i \langle \chi | i \rangle \langle i | \phi \rangle$$

Warning: A summation convention is also sometimes used, such that when a state symbol appears twice, first as a ket, then as a bra, it is assumed to be summed over a complete set of orthonormal basis states. The expression above is then further abbreviated to $\langle \chi | i \rangle \langle i | \phi \rangle$. This convention can be confusing and will not be used in these notes.

Compare this with the vector dot product formula

$$\mathbf{b} \cdot \mathbf{a} = b_x a_x + b_y a_y + b_z a_z = \sum_i (\mathbf{b} \cdot \mathbf{e}_i) (\mathbf{e}_i \cdot \mathbf{a})$$

where \mathbf{e}_i are the unit vectors in x, y and z directions. Just as any vector can be expressed as a linear combination of \mathbf{e}_i , so any quantum state can be expressed as a linear combination of basis states i . There are certain conditions on the basis states, e.g. they must be ‘orthonormal’ $\langle j | i \rangle = \delta_{ij}$ just as $\mathbf{e}_i \cdot \mathbf{e}_j = \delta_{ij}$. Just as the three Cartesian vectors span a three dimensional space, so the many basis states span a many-dimensional space. In some cases (e.g. Fourier expansions, hydrogen wavefunctions) there are an infinite number of basis states which are therefore related to spanning an infinite-dimensional space. Mathematicians call these ‘Hilbert spaces’. Any state ϕ can thus be viewed as a vector in a multi-dimensional space, where each dimension corresponds to one of the basis functions. It is thus common to use the words eigenstate and eigenvector interchangeably to refer to $|\phi\rangle$. Even before the discovery of quantum mechanics, mathematicians had solved many of the problems in this area.

In Dirac notation we have two quantities, the bra and the ket, whereas in vector algebra we have only one, this is because there is not an exact analogy to commutation for Dirac brackets: $\langle \chi | \phi \rangle = \langle \phi | \chi \rangle^*$ includes taking a complex conjugate. Consider manipulating the bras and kets. We can write a vector in terms of its components thus

$$\mathbf{A} = \sum_i \mathbf{e}_i (\mathbf{e}_i \cdot \mathbf{A})$$

where $(\mathbf{e}_i \cdot \mathbf{A})$ is the amount of \mathbf{A} along the \mathbf{e}_i axis; the components. The quantities on either side of the equation are not numbers but *vectors*. We can generate a whole algebra based on vectors.

Likewise we can write a state thus: $|\phi\rangle = \sum_i |i\rangle \langle i | \phi \rangle$

where $\langle i | \phi \rangle$ is the amount of ϕ along the i basis state; the components or *expansion coefficients*. The quantities on each side of this equation are not numbers but *functions*. ϕ is a normalised wavefunction iff $\sum_i |\langle i | \phi \rangle|^2 = 1$. We can then generate a whole algebra based on bras and kets.

For any different complete sets of basis states i and j , we can write: $|\phi\rangle = \sum_j |j\rangle \langle j | \phi \rangle$, and $\langle \phi | = \sum_i \langle i | \langle i | \phi \rangle$. Expansions in i and j are called different *representations* of ϕ . This is very

similar to using different coordinate systems: the bases i and j are analogous to two sets of axes rotated with respect to one another. We might choose complete set of wavefunctions as a representation which includes ϕ , just as we sometimes choose axes such that some special vector points along the z -axis.

Going even further, the expansion in a basis can be done for any $|\phi\rangle$, so we can dispense with $|\phi\rangle$ and write:

$$1 = \sum_i |i\rangle\langle i|, \text{ the unit operator}$$

All this means is that in any equation you can always proceed by breaking the states down into a complete, orthonormal set of basis functions. This may be useful when dealing with a Hamiltonian for which the eigenstates i with eigenenergies E_i are already known. A general mixed state $|\phi\rangle$ has energy:

$$\langle\phi|H_0|\phi\rangle = \sum_i \sum_j \langle\phi|i\rangle\langle i|H_0|j\rangle\langle j|\phi\rangle = \sum_i |\langle\phi|i\rangle|^2 E_i \quad \text{since for } i \neq j \quad \langle j|E_i|i\rangle, \langle j|i\rangle = 0$$

So we could use the solution to an easier problem (the eigenvalue problem, which we need solve only once per Hamiltonian) so that we never need to apply the complicated Hamiltonian to the complicated mixed state! This is a very useful trick - reformulating a problem so that we can make use of some work that has already been done. In this case the single, hard, problem of finding the energy of a mixed state is changed to the many, easier, problems of finding the energy of the eigenstates and the amount of each eigenstate in the mixed state.

1.8 Using Bras to pick Kets

One of the most useful algebraic tricks in quantum mechanics is to multiply a sum of terms by a complex conjugate wavefunction, and integrate the product over all space. Orthogonality often means that this procedure can be used to ‘pick’ a single term from the sum. In Dirac notation this procedure simply becomes applying $\langle i_m|$.

For example, if we have an expansion of a mixed state Φ in eigenstates i_n : $\hat{H}|\Phi\rangle = \sum_n \hat{H}|i_n\rangle\langle i_n|\Phi\rangle$, we can remove the sum by $\langle i_m|$:

$$\langle i_m|\hat{H}|\Phi\rangle = \langle i_m|\sum_n \hat{H}|i_n\rangle\langle i_n|\Phi\rangle = E_m\langle i_m|\Phi\rangle$$

This works because $\langle i_m|\hat{H}|i_n\rangle = E_m\delta_{nm}$; it is analogous to taking components of a vector.

1.9 Good quantum numbers

It is normal to think of the eigenvalues as labelling states. In that case they are just called quantum numbers. A set of eigenvalues from a complete commuting set of operators are called good quantum numbers. The eigenvalues from a non-commuting operator are a bad quantum numbers, because their values cannot be known simultaneously.

This is not quite as simple as it seems. In real systems the Hamiltonian may contain many small terms (perturbations) which may not commute with the operators which commute with the unperturbed Hamiltonian. Although in principle the quantum numbers are no longer good, in practice they are often used.

An example of this is in spin-orbit coupling of angular momenta in many-electron atoms. Here $L_z = \sum_i l_{iz}$ is a good quantum number in the absence of spin-orbit coupling, but \hat{l}_{iz} does not commute with the spin orbit coupling operator $\sum_i \hat{l}_i \cdot \hat{s}_i$. Thus for light atoms, where spin-orbit coupling is weak, L_z is often used although it is not strictly a good quantum number.

2 Review: Time-Independent Non-degenerate Perturbation Theory

There's nothing new in this section, it's simply an alternative derivation to the one you saw last year in Junior Honours. If you preferred that derivation, feel free to read over those notes, the results are the same!

2.1 Small changes to the Hamiltonian

There are very few problems in quantum mechanics which can be solved exactly. However, we are often interested in the effect of a small change to a system, and in such cases we can proceed by assuming that this causes only a small change in the eigenstates. *Perturbation theory* provides a method for finding approximate energy eigenvalues and eigenfunctions for a system whose Hamiltonian is of the form

$$\hat{H} = \hat{H}_0 + \hat{V}$$

where \hat{H}_0 is the 'main bit' of the Hamiltonian of an exactly solvable system, for which we know the eigenvalues, E_n , and eigenfunctions, $|n\rangle$, and \hat{V} is a *small*, time-independent perturbation. \hat{H} , \hat{H}_0 and \hat{V} are Hermitean operators. Using perturbation theory, we can get approximate solutions for \hat{H} using as basis functions eigenstates of the similar, exactly solvable system \hat{H}_0 .

Assuming that \hat{H} and \hat{H}_0 possess discrete, non-degenerate eigenvalues only, we write

$$\hat{H}_0 |n_i\rangle = E_i |n_i\rangle$$

in Dirac notation. The states $|n_i\rangle$ are orthonormal. WLOG, consider a state $i = 0$: the effect of the perturbation will be to modify the state and its corresponding energy slightly; The eigenstate $|n_0\rangle$ will become $|\phi_0\rangle$ and E_0 will shift to $E_0 + \Delta E_0$, where

$$\hat{H} |\phi_0\rangle = (E_0 + \Delta E_0) |\phi_0\rangle$$

WLOG, expanding $|\phi_0\rangle$ in the basis set $|n_i\rangle$ with coefficients c_{i0} and premultiplying by $\langle n_0|$

$$\langle n_0|(\hat{H}_0 + \hat{V}) \sum_{i=0,\infty} c_{i0} |n_i\rangle = (E_0 + \Delta E_0) \langle n_0| \sum_{i=0,\infty} c_{i0} |n_i\rangle$$

Which after a little algebra and cancellation yields the exact result:

$$\Delta E_0 = \langle n_0|\hat{V}|n_0\rangle + \sum_{i=1,\infty} (c_{i0}/c_{00}) \langle n_0|\hat{V}|n_i\rangle \quad (1)$$

Similarly, expanding $|\phi_0\rangle$ in the basis set $|n_i\rangle$ and premultiplying by another state $\langle n_k|$

$$\langle n_k|(\hat{H}_0 + \hat{V}) \sum_{i=0,\infty} c_{i0} |n_i\rangle = (E_0 + \Delta E_0) \langle n_k| \sum_{i=0,\infty} c_{i0} |n_i\rangle$$

leading to $|\phi_0\rangle$ having a component of $|n_k\rangle$

$$c_{k0}(E_0 + \Delta E_0 - E_k) = \sum_{i=0,\infty} c_{i0} \langle n_k|\hat{V}|n_i\rangle \quad (2)$$

Note that although we have denoted the unperturbed state as $|n_0\rangle$, it is not necessarily the ground state.

2.2 First order energy shifts

In first order perturbation theory, we assume that the change in the wavefunction is small, i.e. $|c_{i0}/c_{00}| \ll 1 \forall i$ and neglect the second term in equation 1 which becomes.

$$\Delta E_0 \approx \langle n_0 | \hat{V} | n_0 \rangle \equiv V_{00}$$

which is one of *the most useful results in quantum mechanics*. It tells us how to calculate the change in the n th energy eigenvalue, to first order:

The shift in energy induced by a perturbation is given to first order by the expectation value of the perturbation with respect to the unperturbed state.

Thus first order time independent perturbation is equivalent to making the approximation that *the wavefunction does not change*. Loosely, this works because the energy depends on the perturbation to first order, but on wavefunction *squared*.

2.3 Mixing of the eigenstates of \hat{H}_0

Turning to equation 2, we make the approximation $c_{i0} \ll c_{00} \approx 1 \forall i \neq 0$ so that the only significant term in the sum comes from $i = 0$, and also that ΔE_0 is negligible compared to the energy difference between states 0 and k :

$$c_{k0} \approx \langle n_k | \hat{V} | n_0 \rangle / (E_0 - E_k) \quad (3)$$

Using these coefficients, we see that the perturbation causes a first-order correction to the energy eigenvector $|n_0\rangle$:

$$|\phi_0\rangle = |n_0\rangle + \sum_{k \neq 0} \frac{\langle n_k | \hat{V} | n_0 \rangle}{(E_0 - E_k)} |n_k\rangle \equiv |n_0\rangle + \sum_{k \neq 0} \frac{V_{k0}}{(E_0 - E_k)} |n_k\rangle$$

Which defines the *matrix element* V_{ij} for $i = k, j = 0$. We speak of the perturbation *mixing the unperturbed eigenfunctions* since the effect is to add to the unperturbed eigenfunction, $|n_0\rangle$, a small amount of each of the other unperturbed eigenfunctions. The denominator suggests that states with similar energies are more strongly mixed, and the “matrix element” determines how the perturbation mixes the states.

Unlike the formula for the energy shift, we are faced in general with evaluating an infinite sum to find the correction to the eigenfunctions.

2.4 Higher Orders

It may turn out that the matrix element V_{00} is zero, often due to symmetry. In this case we must consider what happens at second order. Going back to equation 1, and using our expression for mixing and assumption $c_{00} \approx 1$

$$\Delta E_0 = 0 + \sum_{i=1,\infty} \langle n_i | \hat{V} | n_0 \rangle \frac{V_{0i}}{(E_0 - E_i)} = \sum_{i=1,\infty} \frac{|V_{i0}|^2}{(E_0 - E_i)}$$

2.5 Notes

- The results in 2.2 2.3 and 2.4 are worth memorising: physicists use them without proof.
- Energy shifts are real numbers, but matrix elements may be complex.
- If the perturbation operator commutes with the Hamiltonian, “Off-diagonal” matrix elements (V_{ij} , $i \neq j$) are zero. Such perturbations change the energy, but not the wavefunction.
- If the perturbation is turned on and off again, the off-diagonal matrix elements determine whether the quantum state is changed.
- To help with notation, we have derived results for perturbation to a state labelled by 0. This is not necessarily the ground state - the above derivation is general.
- For the first-order changes to the eigenfunction to be small we must have:

$$\langle n_k | \hat{V} | n_0 \rangle \equiv V_{k0} \ll |(E_0 - E_k)| \quad \text{for all } k \neq n$$

- Similarly, we require that the level shift be small compared to the level spacing in the unperturbed system:

$$|\Delta E_0| \ll \min |(E_0 - E_k)|$$

- These conditions may break down *if there are degeneracies in the unperturbed system*. However, we need only assume that the *particular energy level whose shift we are calculating is non-degenerate* for the preceding analysis to be correct.
- The first order corrected wavefunctions are not fully normalised.
- The second order term always lowers the energy of the ground state.

2.6 Example

Consider a simple harmonic oscillator in its ground state, to which we apply a perturbation $\hat{V} = \lambda x^2$. We know the unperturbed wavefunction $|n_0\rangle = [m\omega_0/\pi\hbar]^{\frac{1}{4}} \exp\{-m\omega_0 x^2/2\hbar\}$, so we can evaluate the first order shift in energy according to the perturbation theory:

$$\Delta E_0 = \langle n_0 | \lambda x^2 | n_0 \rangle = \lambda \sqrt{m\omega_0/\pi\hbar} \int x^2 \exp\{-m\omega_0 x^2/\hbar\} dx = \frac{\lambda}{2} \frac{\hbar}{m\omega_0}$$

In this case we know the exact shift, since the perturbation is simply an additional harmonic potential, giving a total $k = m\omega_0^2 + 2\lambda$ and an exact ground state energy of $\frac{1}{2}\hbar\sqrt{\omega_0^2 + 2\lambda/m}$. It is easy to verify that to first order in λ these expressions are identical.

To determine the amount of mixing of states, we need to evaluate matrix elements like $\langle n_0 | \lambda x^2 | n_i \rangle$. We won't evaluate these here, but we will note that for odd i the integral is zero - the symmetric perturbation only mixes in symmetric excited states.

3 Dealing with Degeneracy

3.1 Time-Independent Degenerate Perturbation Theory

We have seen how we can find approximate solutions for a system whose Hamiltonian is of the form

$$\hat{H} = \hat{H}_0 + \hat{V}$$

When we assumed that \hat{H} and \hat{H}_0 possess discrete, non-degenerate eigenvalues only. This led to a mixing of states where

$$|\phi_0\rangle = |n_0\rangle + \sum_{k \neq 0} \frac{V_{k0}}{(E_0 - E_k)} |n_k\rangle$$

Clearly, if $E_0 = E_k$ this diverges. As do the higher order energy shifts (see 2.4). Thus for the degenerate case we cannot associate a particular xperturbed state $|\phi_0\rangle$ with a particular unperturbed state $|n_0\rangle$: we need to take a different approach. In fact, the approximation we make is completely different: we assume that the small perturbation *only mixes those states which are degenerate*. We then solve the problem exactly for that subset of states.

Assume that \hat{H}_0 possesses N degenerate eigenstates $|m\rangle$ with eigenvalue E_{deg} . It may also possess non-degenerate eigenstates, which can be treated separately by non-degenerate perturbation theory. We write a perturbed eigenstate $|\phi_j\rangle$ as an linear expansion in the unperturbed degenerate eigenstates only:

$$|\phi_j\rangle = \sum_i |m_i\rangle \langle m_i | \phi_j \rangle = \sum_i c_{ji} |m_i\rangle$$

Where i here runs over degenerate states only. The TISE now becomes:

$$[\hat{H}_0 + \hat{V}] |\phi_j\rangle = [\hat{H}_0 + \hat{V}] \sum_i c_{ni} |m_i\rangle = E_j \sum_i c_{ni} |m_i\rangle$$

but we know that for all degenerate eigenstates $\hat{H}_0 |m_i\rangle = E_{deg} |m_i\rangle$. So we obtain:

$$\sum_i c_{ji} \hat{V} |m_i\rangle = (E_j - E_{deg}) \sum_i c_{ji} |m_i\rangle$$

premultiplying by some unperturbed state $\langle m_k |$ gives

$$\sum_i c_{ji} [\langle m_k | \hat{V} | m_i \rangle - \delta_{ik} (E_j - E_{deg})] = 0$$

We can get a similar equation from each unperturbed state $|m_k\rangle$. We thus have an eigenvalue problem: the eigenvector has elements c_{ji} and the eigenvalues are $\Delta E_j = E_j - E_{deg}$. Writing the matrix elements between the i^{th} and k^{th} unperturbed degenerate states as $V_{ik} \equiv \langle m_i | \hat{V} | m_k \rangle$ we recover the determinantal equation:

$$\begin{vmatrix} V_{11} - \Delta E_j & V_{12} & \dots & V_{1N} \\ V_{21} & V_{22} - \Delta E_j & \dots & V_{2N} \\ \dots & \dots & \dots & \dots \\ V_{N1} & V_{N2} & \dots & V_{NN} - \Delta E_j \end{vmatrix} = 0$$

The N eigenvalues obtained by solving this equation give the shifts in energy due to the perturbation, and the eigenvectors give the perturbed states $|\phi\rangle$ in the unperturbed, degenerate basis set $|m\rangle$.

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premultiplying by some unperturbed state $\langle m_k |$ gives

$$\sum_i c_{ji} [\langle m_k | \hat{V} | m_i \rangle - \delta_{ik} (E_j - E_{deg})] = 0$$

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The N eigenvalues obtained by solving this equation give the shifts in energy due to the perturbation, and the eigenvectors give the perturbed states $|\phi\rangle$ in the unperturbed, degenerate basis set $|m\rangle$.

3.2 Notes

- The perturbed eigenstates of \hat{H} are linear combinations of degenerate eigenstates of \hat{H}_0 . This means that they too are eigenstates of \hat{H}_0 from a different eigenbasis.
- If \hat{H}_0 is compatible with \hat{V} , i.e. $[\hat{H}_0, \hat{V}] = 0$, then there is no mixing with non-degenerate states and the analysis above is exact.
- Notice how the mathematics mimics the quantum mechanics. Without the perturbation the eigenbasis of \hat{H}_0 is not unique. When we try to determine its energy shift we find a matrix equation which can *only* be solved for *specific* values of ΔE_j . These ΔE_j in turn correspond to specific choices for the coefficients c_{ji} , i.e. particular linear combinations of the unperturbed states. Thus to solve the equations we are forced to collapse the wavefunction onto an eigenstate of \hat{V} . V_{ki} is a Hermitian matrix, and consequently has real eigenvalues.

3.3 Example of degenerate perturbation theory: Stark Effect in Hydrogen

The change in energy levels in an atom due to an external electric field is known as the Stark effect. The perturbing potential is thus $\hat{V} = eEz = eEr \cos \theta$. Ignoring spin, we examine this effect on the fourfold degenerate $n=2$ levels. We will label these by their appropriate quantum number: $|l, m\rangle$.

$$\begin{aligned} u_{00} &= (8\pi a_0^3)^{-1/2} (1 - r/2a_0) e^{-r/2a_0}; & u_{10} &= (8\pi a_0^3)^{-1/2} (r/2a_0) \cos \theta e^{-r/2a_0} \\ u_{11} &= (\pi a_0^3)^{-1/2} (r/8a_0) \sin \theta e^{i\phi} e^{-r/2a_0} & u_{1-1} &= (\pi a_0^3)^{-1/2} (r/8a_0) \sin \theta e^{-i\phi} e^{-r/2a_0} \end{aligned}$$

From the analysis above, we need to calculate the matrix elements.

$$V_{lm, l'm'} = \langle l, m | eEz | l', m' \rangle = eE \int \int \int u_{lm}^*(r \cos \theta) u_{l'm'} r^2 \sin \theta d\theta d\phi dr$$

It turns out that many of these are zero, since if any of the integrals are zero their product will be. Looking first at parity, it is clear that eEz has odd parity ($eE(r) \cos(\pi - \theta) = -eEr \cos \theta$), u_{00} has even parity and u_{1m} have odd parity. Since the integral over all space of any odd function is zero, $V_{00,00} = V_{1m,1m'} = 0$. Secondly, $\int_0^{2\pi} e^{\pm i\phi} d\phi = 0$, so $V_{00,11} = V_{00,1-1} = V_{11,00} = V_{1-1,00} = 0$.

Since the perturbation is real, $V_{00,10} = V_{10,00}$ and the only remaining non-zero matrix element is:

$$\langle 00 | eEr \cos \theta | 10 \rangle = (8\pi a_0^3)^{-1} \int_0^{2\pi} d\phi \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^\infty (1 - r/2a_0) e^{-r/a_0} r^4 / 2a_0 dr = -3eEa_0$$

This is best solved as a matrix problem, the determinantal equation is then:

$$\begin{vmatrix} -\Delta E & -3eEa_0 & 0 & 0 \\ -3eEa_0 & -\Delta E & 0 & 0 \\ 0 & 0 & -\Delta E & 0 \\ 0 & 0 & 0 & -\Delta E \end{vmatrix} = (\Delta E)^4 - (\Delta E)^2 (3eEa_0)^2 = 0$$

The solutions to this are $\Delta E = \pm 3eEa_0, 0, 0$. The degeneracy of the states u_{11} and u_{1-1} is not lifted, but the new non-degenerate eigenstates corresponding to $\Delta E_n = \pm 3eEa_0$ are mixtures, $(u_{00} \mp u_{10})/\sqrt{2}$. Consequently, the spectral line corresponding to the $n = 2 \rightarrow n = 1$ Lyman- α transition is split into three if the hydrogen atom is in an electric field.

A curious aspect of these eigenstates is that they are not eigenstates of \mathbf{L}^2 , although they are eigenstates of L_z . Nor do they have definite parity. In an electric field, therefore, the total angular

momentum is not a good quantum number. Note that this effect is specific to hydrogen, since in other elements the s and p levels are not degenerate.

Experimental results confirm this theory beautifully - the splitting of levels in hydrogen varies linearly with the applied field strength, while in all other atoms it varies quadratically: the first order perturbation is zero.

Looking at the electrostatics: the energy of a spherically symmetric charge density in a uniform field is clearly independent of orientation. To have any orientation dependence the object must have a dipole moment. The combination of $2s$ and $2p$ wavefunctions achieves this.

3.4 Symmetry and Degeneracy

In real systems degeneracy almost always related to symmetry. In general if the probability density has lower symmetry than the Hamiltonian, the wavefunction will be degenerate.

There is a clear physical reason behind this. Consider the $2p_x$ orbital in hydrogen: it has a lobe along the x -axis. However, there is no measurable quantity which defines an x -axis - the coordinate system is just introduced by physicists to help solve the equations. The lobe could just as well point in the y or z or $(27, 43.2, -12)$ direction. Thus the p_x orbital has lower symmetry than the Hamiltonian (spherically symmetric potential), and is degenerate with p_y and p_z . Likewise the spin: we talk about 'spin up', but there is no way to define 'up' from the Hamiltonian. Thus there is degeneracy between spin states 'up' and 'down'.

If we reduce the symmetry of the Hamiltonian, we now 'lift' the degeneracy. (i.e. the levels no longer have the same energy). For example, an applied magnetic field defines an axis and lowers the symmetry of the Hamiltonian. If the field is weak, we can use perturbation theory and assume we still have p orbitals (Zeeman effect). Now, the orbitals must be eigenstates not only of \hat{H}_0 , but also of $\mu \cdot \mathbf{B}$ where μ is the magnetic dipole moment. The degenerate energy level splits into several different energy levels, depending on the relative orientation of the moment and the field: The degeneracy is lifted by the reduction in symmetry.

3.5 Time-variation of expectation values: Degeneracy and constants of motion

The time variation of the expectation value of an operator \hat{A} which commutes with the Hamiltonian is:

$$\frac{d}{dt}\langle\Phi|\hat{A}|\Phi\rangle = \int d^3r \frac{d\Phi^*}{dt} \hat{A}\Phi + \Phi^* \hat{A} \frac{d\Phi}{dt}$$

but since $i\hbar \frac{d\Phi}{dt} = \hat{H}\Phi$ and $-i\hbar \frac{d\Phi^*}{dt} = \hat{H}^*\Phi^*$

$$-i\hbar \frac{d}{dt}\langle\Phi|\hat{A}|\Phi\rangle = \int (\hat{H}^*\Phi^* \hat{A}\Phi - \Phi^* \hat{A} \hat{H}\Phi) d^3r = \langle\Phi|[\hat{H}, \hat{A}]|\Phi\rangle$$

Where we also use the fact that \hat{H} is Hermitian. Thus if \hat{H} commutes with \hat{A} ($[\hat{H}, \hat{A}] = 0$), the expectation value of A is independent of time. It is a conserved quantity.

As we have seen above, if we have degenerate eigenstates of the Hamiltonian, \hat{H} , then there must be some other operator \hat{A} which commutes with the Hamiltonian for which there are energy-degenerate eigenstates with different eigenvalues A . These eigenvalues, A , are then constants of the motion. Moreover, if Φ is an eigenfunction of \hat{H} , then $\hat{A}\Phi$ is also an eigenfunction of \hat{H} .

$$\hat{H}(\hat{A}\Phi) = \hat{A}\hat{H}\Phi = \hat{A}(E\Phi) = E(\hat{A}\Phi)$$

There is a three way link between symmetry, degeneracy and conserved quantities.

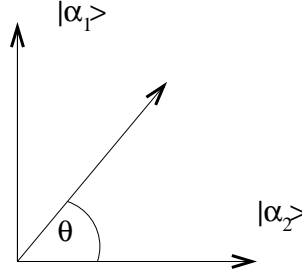


Figure 1: Any linear combination of two degenerate eigenstates produces another eigenstate.

3.6 Wavefunction Collapse onto degenerate levels

Refer back to the postulates of quantum mechanics: We know that acting with an operator \hat{A} on an eigenstate $|\alpha_n\rangle$ of that operator gives us an eigenvalue A_n , which corresponds to a measurable quantity.

There is no guarantee that $|\alpha_n\rangle$ is the only eigenstate of \hat{A} which has this eigenvalue (e.g. energy levels in hydrogen). Different states with the same eigenvalue are referred to as degenerate.

Assume we find two orthogonal, degenerate eigenstates of \hat{A} : $|\alpha_1\rangle$ and $|\alpha_2\rangle$. i.e. $\hat{A}|\alpha_1\rangle = A_1|\alpha_1\rangle$ and $\hat{A}|\alpha_2\rangle = A_1|\alpha_2\rangle$. We also see that

$$\hat{A}(\cos\theta|\alpha_1\rangle + \sin\theta|\alpha_2\rangle) = A_1(\cos\theta|\alpha_1\rangle + \sin\theta|\alpha_2\rangle)$$

for any θ . We use $\cos\theta$ for the expansion instead of the normal c_i to emphasise the similarity between eigenstates and vectors. It also allows for easy normalisation since $\cos^2\theta + \sin^2\theta = 1$.

Thus any linear combination of degenerate eigenstates produces another eigenstate. There is still only twofold degeneracy, because there are only two orthogonal states, $(\sin\theta|\alpha_1\rangle - \cos\theta|\alpha_2\rangle)$ being the other one. The complete set of orthonormal eigenstates for \hat{A} is thus not a unique quantity, since we can choose any θ to generate a pair of degenerate eigenstates.

A consequence of this is that when a measurement is made of \hat{A} which finds A_1 , there is not a complete collapse of the wavefunction.

Consider measuring observable A in a system in a general state $|\Phi\rangle$. By expanding $|\Phi\rangle$ in the eigenstates of \hat{A} : $|\Phi\rangle = \sum_i c_i|\alpha_i\rangle$ we find the probability that the measurement will yield result A_1 is

$$|\langle\alpha_1|\Phi\rangle|^2 + |\langle\alpha_2|\Phi\rangle|^2 \equiv |c_1|^2 + |c_2|^2$$

The measurement has determined that we are either in state α_1 or α_2 , but not which. Thus there is a partial collapse of the wavefunction onto a linear combination of them:

$$(\cos\theta|\alpha_1\rangle + \sin\theta|\alpha_2\rangle); \quad \cos\theta = \frac{c_1}{\sqrt{|c_1|^2 + |c_2|^2}}$$

which is itself an eigenvector of \hat{A} .

Thus, in the case of degenerate final states, the final wavefunction after the measurement *does* depend on the initial wavefunction. The generalisation of this to the case of many degenerate states is straightforward.

4 Degeneracy, Symmetry and Conservation Laws

4.1 Distinguishing between eigenstates, Quantum numbers as labels

How can we distinguish between quantum states $|\alpha_n\rangle$ which have degenerate values of A ? The obvious way is to measure the quantised observables and use them to label the state. We must be sure not to make measurements which change the state. Thus all measurements should correspond to commuting operators (Compatible observations: see QP3). In the non-degenerate case measuring energy is sufficient, but in hydrogen, for example, we used quantum numbers n (for energy, operator \hat{H}), l (for total angular momentum, $\hat{\mathbf{L}}^2$) and m_l (one component of angular momentum, \hat{L}_z).

Continuing the example of twofold degeneracy (3.6), suppose that some operator \hat{B} is compatible with \hat{A} . This means that $[\hat{A}, \hat{B}] = 0$ and \hat{A} and \hat{B} have a common eigenbasis. i.e. some θ and $\theta + \pi/2$ give eigenstates of both \hat{A} and \hat{B} in the form $|\alpha(\theta)\rangle = (\cos \theta |\alpha_1\rangle + \sin \theta |\alpha_2\rangle)$.

To find the appropriate value of θ , we have a similar problem to that encountered in 3.1 and must solve for the eigenvectors of:

$$\begin{pmatrix} \langle \alpha_1 | \hat{B} | \alpha_1 \rangle & \langle \alpha_1 | \hat{B} | \alpha_2 \rangle \\ \langle \alpha_2 | \hat{B} | \alpha_1 \rangle & \langle \alpha_2 | \hat{B} | \alpha_2 \rangle \end{pmatrix}$$

The eigenvalues of this equation are the quantised measurable values of \hat{B} . If both of these are equal, there must be another measurable C which will distinguish the two states.

The generalisation to many degenerate levels is straightforward. If there are n orthogonal degenerate eigenstates of \hat{A} , (therefore an n -dimensional space in which every unit vector is an eigenstate of \hat{A}), compatibility of eigenbases means there are at least n eigenstates of \hat{B} . It is now possible that all these have different B eigenvalues, or that at least two have the same eigenvalue, in which case if we want a specific set of orthogonal eigenstates, we must look for another compatible operator \hat{C} .

When the set of operators is sufficiently large that there is a unique set of eigenvalues for each eigenstate, we call it a complete commuting set of operators. An example is \hat{H} , $\hat{\mathbf{L}}^2$, \hat{S}_z and \hat{L}_z in hydrogen. The complete commuting set is not unique for a given Hamiltonian, for hydrogen we could have used \hat{H} , $\hat{\mathbf{L}}^2$, \hat{S}_x and \hat{L}_x or \hat{H} , $\hat{\mathbf{L}}^2$, \hat{J} and \hat{L}_z . If one of the quantum numbers can be written in terms of the others then it is redundant. If two of the quantum numbers come from non-commuting operators, then the set does not define a state since the full set of measurements could not be performed without changing the wavefunction.

4.2 Example

Consider the 2D harmonic oscillator $V_0 = \frac{1}{2}m\omega^2(x^2 + y^2)$. If we measure the energy and find it to be $2\hbar\omega$, then the state could be $|n_x = 1, n_y = 0\rangle$ or $|n_x = 0, n_y = 1\rangle$ or any linear combination. To fully define any state we require any two quantum numbers: n_x , n_y and $E = (n_x + n_y + 1)\hbar\omega$.

Suppose we measure the energy and find $3\hbar\omega$: there is a *partial* collapse of the wavefunction and there are three degenerate possibilities. Suppose we then apply a perturbation $\Delta V = \lambda x^2$ (see 2.6). This breaks the symmetry and collapses the wavefunction onto either $|1, 1\rangle$, $|2, 0\rangle$ or $|0, 2\rangle$. The perturbation matrix (see 3.1) $\langle n_x, n_y | \Delta V | n_x, n_y \rangle$ is diagonal provided we choose the basis with x along the direction of the perturbation, and it has eigenvalues $(n_x + \frac{1}{2})\lambda\hbar/m\omega$. If we then measure the energy and find $E = 3\hbar\omega + \lambda\hbar/2m\omega$ then we know that the state is $|0, 2\rangle$: a *complete* collapse onto a single wavefunction.

Aside: Consider mixing with the non-degenerate states. By symmetry $\langle 1, 0 | \lambda x^2 | 2, 0 \rangle = 0$: the perturbation does not mix $n_x = 0$ and $n_x = 1$ states, nor does it affect n_y (see 2.3). Thus applying the perturbation may induce a transition from $|0, 2\rangle$ to $|2, 2\rangle$, $|4, 2\rangle$ etc. but not to $n_x = \text{odd}$ or $n_y \neq 2$. This gives rise to selection rules

4.3 Translational Symmetry and Conservation of Momentum

Consider a transformation operator in 1 dimension \hat{D} which acts on the coordinates of a system as a displacement $\hat{D}[f(x)] = f(x+l)$. The eigenfunctions of \hat{D} satisfy $\hat{D}|\phi(x)\rangle = d|\phi(x)\rangle = |\phi(x+l)\rangle$. The general solutions to this equation are $\phi(x) = e^{ikx}u(x)$ where $u(x)$ satisfies $u(x) = u(x+l)$ and k is complex.

This kind of translational symmetry exists when we have a crystal structure. Now consider a 1D closed loop of N atoms: Uniqueness of the wavefunction requires that $\phi(x) = \phi(x + Nl) \Rightarrow e^{ikx} = e^{ik(x+Nl)}$. Thus possible wavefunctions must have real k and the form

$$\phi(x) = e^{2\pi nix/Nl}u(x); \quad k = 2\pi n/Nl$$

The momentum of this state is given by:

$$-i\hbar \int \phi^*(x) \frac{d\phi(x)}{dx} dx = \int \phi^*(x) \left[\frac{2\pi\hbar n}{Nl} + \frac{u'(x)}{u(x)} \right] \phi(x) dx$$

The RHS first term gives is the familiar $\hbar k$, which we associate with the momentum. If $u(x)$ has some definite parity, then $u'(x)$ will have opposite parity and the second term will be the integral of an odd function (i.e. zero by symmetry). Thus k is a quantum number associated with translational symmetry, which in turn has an operator \hat{D} which commutes with the Hamiltonian and is thus a constant of the motion. Translational symmetry is associated with conservation of momentum.

For which the TISE, with the atom described by a potential $V(x)$, and a particular value of k , can be written

$$\hat{H}_k u_k(x) = \frac{\hbar^2}{2m} \left[\left(k - i \frac{d}{dx} \right)^2 + V(x) \right] u_k(x) = E_k u_k(x)$$

since the phase has been eliminated, we simply have a particle in a fixed volume $u_k(x) = u_k(x+l)$, which means a series of discrete energy levels (bands). Thus all states can be labelled by k and a band index n .

We can write the semiclassical group velocity of the wavefunction as

$$v_g = \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{dE}{dk}$$

using $E = \hbar\omega$. A formal proof using the velocity operator gives the same result for the velocity. Assuming that E does vary with k , this means we have a time-independent state which nevertheless has a permanent, non-zero velocity through the lattice.

4.4 Application - electron in a crystalline solid

The above is the 1D statement of Bloch's Theorem, the basis of study of electrons in solids. If we imagine applying an electric field (\mathcal{E}) in the x -direction, then the rate at which work is done is:

$$-e\mathcal{E}v_g = \frac{dE}{dt} = \frac{dE}{dk} \frac{dk}{dt}$$

Using the expression for v_g we find that the rate of change of $\hbar k$ is proportional to the external force, rather like Newton's second law.

$$-e\mathcal{E} = F = \hbar \frac{dk}{dt}$$

If we now consider acceleration:

$$a = \frac{dv_g}{dt} = \frac{dv_g}{dk} \frac{dk}{dt} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} F$$

we find a quantity $\hbar^2 / \frac{d^2 E}{dk^2}$ which is known as the *effective mass*, relating external force to acceleration in a solid, and allowing us to avoid further consideration of the effect of the lattice.

4.5 The Kronig-Penney Model

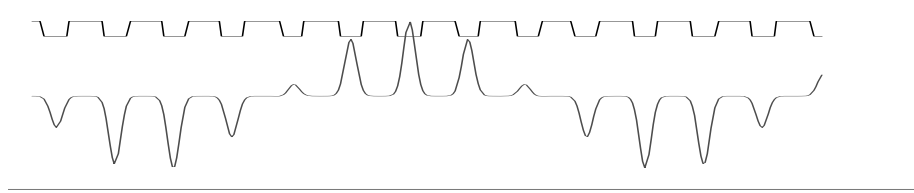


Figure 2: The Kronig-Penney potential and a Bloch function

In 4.1 $u(x)$ is still completely general. The *Kronig-Penney model* considers a periodically repeating square potential defined in one cell by $V(x) = 0$ ($0 < x < b$); $V(x) = V_0$ ($b < x < l$), then we can solve for $u(x)$ in one cell. Like the finite square well, this is a tedious boundary condition problem where matching value and slope of the wavefunction at the potential edge gives a 4x4 matrix to diagonalise. The details are given in wikipedia(!) and lead to an equation the LHS of which is drawn below:

$$\cos k_1 b \cos k_2(l - b) - \frac{k_1^2 + k_2^2}{2k_1 k_2} \sin k_1 b \sin k_2(l - b) = \cos kl$$

where $k_1 = \sqrt{2mE}/\hbar$ and $k_2 = \sqrt{2m(E - V_0)}/\hbar$, the appropriate free particle wavevectors, thus for $E < V_0$, k_2 is imaginary. As the figure shows, multiple solutions are possible for all k , giving certain “bands” of energy, but not others.

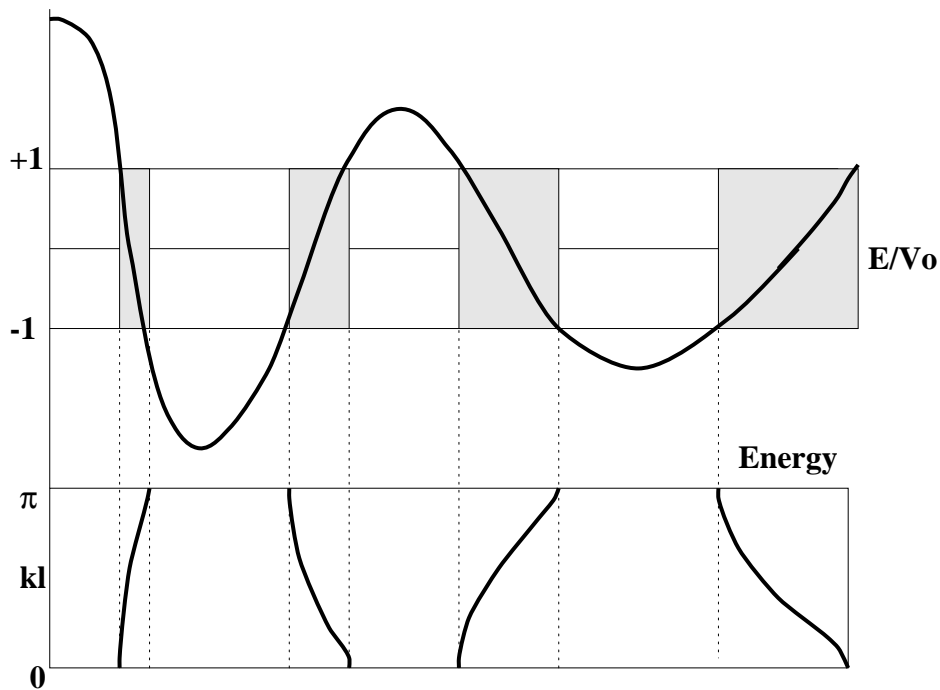


Figure 3: Graph of function arising from multiple square-well problem: Allowed energy solutions exist only where $|\cos kl| \leq 1$.

The key point about this equation is that it cannot be solved for certain values of E , around $k_1 b = m\pi$. A plot of the left hand side of the equation against E/V_0 illustrates this, solutions for some value of k can be found only in the shaded regions of E . Moreover each shaded region contains N allowed $k = 2\pi n/Nl$ values. Thus if each atom contributes two electrons the lower ‘valence’ band will be filled (one of each spin in each state) and the upper ‘conduction’ band will be empty. To get an electron to move (change to a different k -state) requires a lot of energy, so this represents an insulator.

In the limit of $V_0 = 0$, we get $k = k_1 = k_2 = \sqrt{2mE}/\hbar$, the free electron result, while for very large $V_0 \gg E$ solutions are possible only for values of E which satisfy $\sin(k_1 b) \approx 0$, i.e. the square well.

The wavefunction is a complex exponential of $k_1 x$ or $k_2 x$, depending on whether it is in a well or not. It is *not* an eigenfunction of the momentum operator. Thus although $\hbar k$ looks like a momentum, it isn’t the eigenvalue of the momentum operator. It is called “crystal momentum” and along with the “effective mass” gives a pair of quantities with which we can apply Newtonian dynamics thinking to a crystal, ignoring the effects of the lattice.

In three dimensions, the topology of the bands becomes much more complicated: this is a topic for solid state physics.

4.6 Radioactive decay and imaginary potentials

If the number of particles in a given state is reduced in time, then the total intensity of that state is reduced. Consider a particle moving in a region of imaginary potential $V(r) = -iV_0$. The TDSE is:

$$i\hbar \frac{\partial}{\partial t} |\Phi, t\rangle = [H_0 - iV_0] |\Phi, t\rangle$$

Assume that the time independent part of the state is an combination of eigenstates of the real part of the Hamiltonian:

$$|\Phi, t\rangle = \sum_n c_n(t) \exp(-iE_n t/\hbar) |\phi_n\rangle; \quad \text{where} \quad H_0 |\phi_n\rangle = E_n |\phi_n\rangle$$

Following the same analysis as for TDSE, premultiplying by $\langle m|$, and for constant V_0 , $V_{mn} = \delta_{mn} V_0$ we obtain:

$$i\hbar \dot{c}_m = -iV_0 c_m \quad \Rightarrow \quad |c_m(t)|^2 = |c_m(0)|^2 e^{-2V_0 t/\hbar}$$

Thus the probability amplitude of the state decreases in time. An imaginary potential can be used to represent destruction of particles, either by absorption (in a scattering process, perhaps) or by radioactive decay. Obviously the ket is not a full description of the system, since that should include information about the decay products. The lifetime of the state is $\tau = \hbar/2V_0$.

Notice that $-iV_0$ is not a Hermitian operator, and so it is not possible to perform a single measurement of half life.

5 Time-dependence

5.1 Time-dependent Hamiltonians

Recall that for a system described by a Hamiltonian, \hat{H}_0 , which is time-independent, the most general state of the system can be described by a wavefunction $|\Psi, t\rangle$ which can be expanded in the energy eigenbasis $\{|n\rangle\}$ as follows:

$$|\Psi, t\rangle = \sum_n c_n \exp(-iE_n t/\hbar) |n\rangle$$

where the coefficients, c_n , are time-independent, and E_n denotes the eigenvalue corresponding to the energy eigenstate $|n\rangle$ of \hat{H}_0 .

When we generalise to the case where the Hamiltonian is of the form

$$\hat{H} = \hat{H}_0 + \hat{V}(t)$$

we can again expand in $|n\rangle$, the time-independent eigenbasis of \hat{H}_0

$$|\Psi, t\rangle = \sum_n c_n(t) \exp(-iE_n t/\hbar) |n\rangle$$

but the coefficients, c_n , will now in general be time-dependent.

The wavefunction satisfies the time-dependent Schrödinger equation;

$$i\hbar \frac{\partial}{\partial t} |\Psi, t\rangle = \hat{H} |\Psi, t\rangle$$

so that we can substitute the expansion of $|\Psi, t\rangle$ to determine the equations satisfied by the coefficients $c_n(t)$. Writing $E_n = \hbar\omega_n$ and denoting the time derivative of c_n by \dot{c}_n we obtain

$$i\hbar \sum_n (\dot{c}_n - i\omega_n c_n) \exp(-i\omega_n t) |n\rangle = \sum_n (c_n \hbar\omega_n + c_n \hat{V}) \exp(-i\omega_n t) |n\rangle$$

which simplifies immediately to give

$$\sum_n (i\hbar \dot{c}_n - c_n \hat{V}) \exp(-i\omega_n t) |n\rangle = 0$$

We now premultiply this equation with another eigenstate of \hat{H}_0 , $\langle m|$, to give

$$i\hbar \dot{c}_m \exp(-i\omega_m t) - \sum_n c_n V_{mn} \exp(-i\omega_n t) = 0$$

giving the following set of coupled, first-order differential equations for the coefficients:

$$\boxed{i\hbar \dot{c}_m = \sum_n c_n V_{mn} \exp(i\omega_{mn} t)}$$

where $\omega_{mn} = \omega_m - \omega_n$ and $V_{mn} = \langle m|\hat{V}|n\rangle$.

This tells us how the coefficient c_m varies with time, i.e. the probability that a measurement will show the system to be in the m^{th} eigenstate. It is exact, but not terribly useful because we must, in general, solve an infinite set of coupled differential equations.

It is worth dwelling on the importance of the quantity V_{mn} . This ‘matrix element’ is an integral which tells us how much the potential \hat{V} mixes states $|m\rangle$ and $|n\rangle$. If it is zero (which it often is, by symmetry) then \hat{V} cannot induce a transition between states $|m\rangle$ and $|n\rangle$.

5.2 Time-dependent Perturbation Theory

Consider the Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{V}(t)$$

where the time dependent part is *small*. We can write the time dependent coefficients c_n

$$c_n(t) = c_n(0) + \Delta c_n(t)$$

Where $c_n(0)$ is the value of c_n at $t=0$. We substitute in the equation for \dot{c}_m derived above to give

$$\dot{c}_m(t) = (i\hbar)^{-1} \sum_n [c_n(0) + \Delta c_n(t)] V_{mn} \exp(i\omega_{mn}t)$$

We can assume that for a perturbation $c_n(0) \gg \Delta c_n(t)$, and ignore the second term. This allows us to obtain the coefficients $c_m(t)$ by integrating the first-order differential equation to give:

$$c_m(t) = (i\hbar)^{-1} \sum_n c_n(0) \int_0^t V_{mn} \exp(i\omega_{mn}t) dt$$

In the special case where the system is known to be in an eigenstate of \hat{H}_0 , say $|k\rangle$, at $t = 0$, then $c_k(0) = 1$ and all other $c_m(0) = 0$, $m \neq k$, giving

$$c_m(t) = (i\hbar)^{-1} \int_0^t V_{mk} \exp(i\omega_{mk}t) dt$$

Thus a system starting in a known eigenstate of the unperturbed system may transform to a different eigenstate through the action of the perturbing potential. Notice that $c_m(t)$ is an integral over time, if we wait a long time, the transition may become more likely.

The probability of finding the system at a later time, t , in the state $|m\rangle$ where $m \neq k$ is given by

$$p_m(t) = |c_m(t)|^2$$

Since we have assumed a small perturbation, this result is only reliable if $p_m(t) \ll 1$. “Small” here applies to both V_{mk} and its integral over time.

5.3 Time-independent Perturbations

The results obtained in the last section can also be applied to the case where the perturbation, \hat{V} , is actually independent of time (strictly, ‘switched on’ at $t=0$).

Again, starting the system in eigenstate $|k\rangle$ of \hat{H}_0 we obtain,

$$\begin{aligned} c_m(t) \Delta c_m(t) &= (i\hbar)^{-1} V_{mk} \int_0^t \exp(i\omega_{mk}t) dt \\ &= \frac{V_{mk}}{\hbar\omega_{mk}} [1 - \exp(i\omega_{mk}t)] \end{aligned}$$

for $m \neq k$, giving for the transition probability

$$p_m(t) = |\Delta c_m(t)|^2 = \frac{|V_{mk}|^2}{\hbar^2} \frac{\sin^2(\omega_{mk}t/2)}{(\omega_{mk}/2)^2}.$$

For sufficiently large values of t , the function

$$f(t, \omega_{mk}) \equiv \frac{\sin^2(\omega_{mk}t/2)}{(\omega_{mk}/2)^2}$$

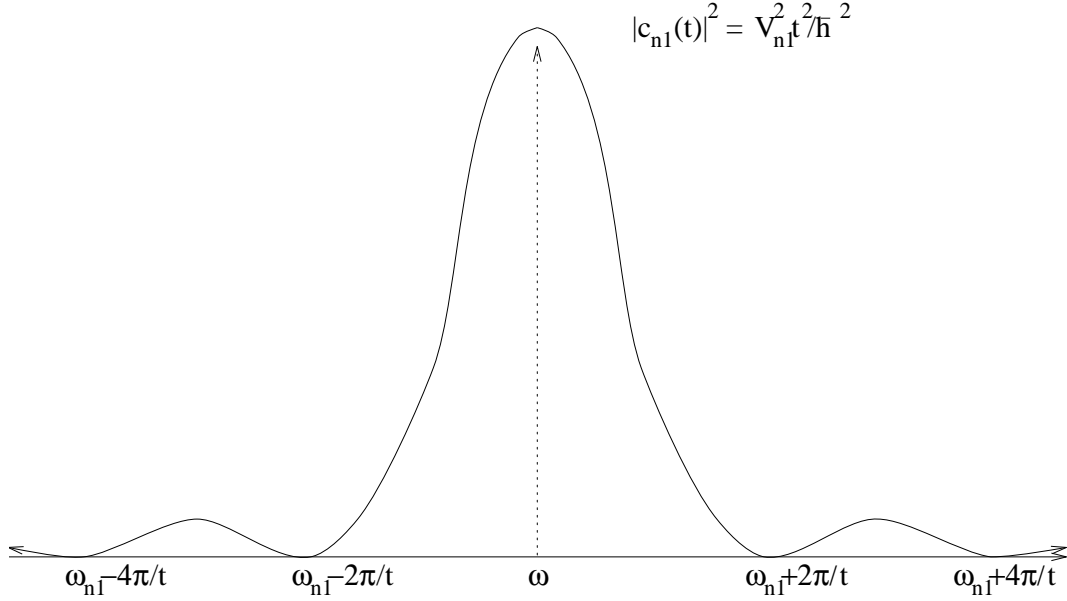


Figure 4: Transition probability as a function of applied harmonic perturbation frequency

consists essentially of a large peak, centred on $\omega_{mk} = 0$, of height t^2 and width $\approx 4\pi/t$, as indicated in Fig. 4. Thus there is only a significant transition probability if $E_m \approx E_k$. That is, if $|\omega_{mk}| < 2\pi/t$.

Note that we are assuming that the system was prepared in some eigenstate of \hat{H}_0 which is not an eigenstate of \hat{V} : if it were, then the matrix element V_{nm} would be zero and $p_m(t) = 0$. Thus although the analysis treats the perturbation as time independent, it is applied to cases where the perturbation is switched on at $t = 0$. Moreover only perturbations which are incompatible with the Hamiltonian can induce transitions.

5.4 Harmonic Perturbation

This is generally useful since by Fourier analysis we can decompose any periodic perturbation into harmonic components.

Let the perturbing potential be $V(\mathbf{r}, t) = V(\mathbf{r}) \cos \omega t$

If the initial state at $t = 0$ is k , and the final state m then

$$c_m \approx \frac{-i}{\hbar} V_{mk} \int_0^t e^{i\omega_{mk}t} \frac{1}{2} (e^{i\omega t} + e^{-i\omega t}) dt = \frac{V_{mk}}{2\hbar} \left(\frac{e^{i(\omega_{mk}-\omega)t} - 1}{\omega_{mk} - \omega} + \frac{e^{i(\omega_{mk}+\omega)t} - 1}{\omega_{mk} + \omega} \right)$$

where V_{mk} is the time independent part of the matrix element $\langle m | \hat{V} | k \rangle$. This function is dominated by the first term in the region around $\omega_{mk} = \omega$, so we can consider only the first term to obtain an estimate for the transition probability:

$$|c_m(t)|^2 = \frac{V_{mk}^2 \sin^2[(\omega_{mk} - \omega)t/2]}{\hbar^2 (\omega_{mk} - \omega)^2} = \frac{1}{4\hbar^2} V_{mk}^2 f(t, \omega_{mk} - \omega)$$

Where the function f is the same as we encountered earlier. Thus an external perturbation at a given frequency most strongly induces transitions between energy levels separated by $\hbar\omega$.

This is another manifestation of an uncertainty principle. If the potential is electromagnetic, the most probable transition is the absorption of a $\hbar\omega_{mk}$ photon as the system changes energy by

$\hbar\omega_{mk}$. But if the transition happens very fast, the peak is broad and the photon could have a wide range of energies, contrariwise, if the transition occurs after a long time the photon frequency is well defined: $\Delta E\Delta t \geq \hbar/2$. This uncertainty gives rise to the ‘natural linewidth’ of a particular transition, and causes a limit to the accuracy of certain experiments. There is a slight difference from the Heisenberg Uncertainty in non-relativistic quantum mechanics because time is not an operator so one cannot define the commutator of time with the Hamiltonian.

Note the extraordinary result that the transition probability at small times is $(V_{mk}^2/4\hbar^2)t^2$. Consider what happens if the state is measured frequently compared to if measurements are made infrequently: frequent measurement tends to inhibit the transition!

5.5 Transitions to a group of states

We are often interested in the situation where transitions take place not to a single final state but to a group, G , of final states with energy in some range about the initial state energy

$$E_k - \Delta E \leq E_m \leq E_k + \Delta E$$

Then the total transition probability is obtained by summing the contributions of all the final states. The number of final states in the interval between E_m and $E_m + dE_m$ is $g(E_m) dE_m$, where the function $g(E_m)$ is known as the *density of final states*. The total transition probability for transitions to G is then given by

$$p_G(t) = \frac{1}{\hbar^2} \int_{E_k - \Delta E}^{E_k + \Delta E} |V_{mk}|^2 f(t, \omega_{mk}) g(E_m) dE_m.$$

For sufficiently large t , and $\Delta E \gg 2\pi\hbar/t$, we observe that essentially the only contributions to the integral come from the energy range corresponding to the narrow central peak of the function $f(t, \omega_{mk})$. Within this range we can neglect the variation of $g(E_m)$ and V_{mk} , which can therefore be taken out of the integral to give

$$p_G(t) = \left[\frac{|V_{mk}|^2}{\hbar^2} g(E_m) \right]_{E_m=E_k} \int_{E_k - \Delta E}^{E_k + \Delta E} f(t, \omega_{mk}) dE_m.$$

Furthermore, we can extend the limits on the integration to $\pm\infty$. Noting that $dE_m = \hbar d\omega_{mk}$ and using the result that

$$\int_{-\infty}^{\infty} \frac{\sin^2 x}{x^2} dx = \pi$$

we obtain for the first-order transition probability

$$p_G(t) = \frac{2\pi t}{\hbar} \left[|V_{mk}|^2 g(E_m) \right]_{E_m=E_k}$$

The transition rate, R , is just the derivative of this with respect to t and is thus given by the so-called Fermi Golden Rule:

$$R = \frac{2\pi}{\hbar} \left[|V_{mk}|^2 g(E_m) \right]_{E_m=E_k}$$

The Fermi Golden Rule is probably the single most widely used result in quantum mechanics. The factor of $\frac{2\pi}{\hbar}$ depends on the choice of perturbing potential, but the $|V_{n1}|^2 g(E_m)$ term appears for any applied perturbation. Be careful about the density of energy states - one sometimes encounters density of frequency states (which differs by a factor of \hbar) or of wavevector states.

It may appear that need to know the density of final states, $g(E_m)$, but this is not always true. In cases where $|V_{mk}| = 0$ transitions are forbidden, and in some cases we can deduce $g(E_m)$ from the relative rates of related transitions.

5.6 Example of Golden rule - beta decay

A nucleus decays via the reaction $n \rightarrow p e^- \bar{\nu}$. to form a electron and antineutrino, releasing energy E_0 .

The simplest form for the matrix element describing nuclear β -decay is given by the so-called Fermi ansatz $V_{mk} = G_F M / \Omega$ where Ω is the normalisation volume for the wavefunctions, $|M|^2 \approx 1$ is the wavefunction overlap between initial and final nuclear states and G_F is a constant.

We can work in the COM reference frame, so the kinetic energy of the nucleus is zero. Momentum is conserved, so the final state has nuclear, electron and neutrino momentum $\mathbf{P} + \mathbf{p} + \mathbf{q} = 0$ while the energy released goes into the electron and neutrino, which for simplicity we treat as massless: $E_0 = E_e + q$ The proton and neutron are heavy compared with the electron and neutrino. Given that momentum must be conserved, the kinetic energy must be concentrated in the lighter particles.

The density of final states for the electron is given by the phase space volume

$$dn = \frac{d^3\mathbf{p} d^3\mathbf{r}}{(2\pi\hbar)^3}$$

with a similar expression for the neutrino. Number of states in a volume of phase space is given by the number of electron states, times the number of neutrino states, provided energy is conserved:

$$dn = \frac{d^3\mathbf{p} d^3\mathbf{r}}{(2\pi\hbar)^3} \frac{d^3\mathbf{q} d^3\mathbf{r}}{(2\pi\hbar)^3} \delta(E_e + q - E_0)$$

Using the relativistic relation $E^2 = p^2 c^2 + m^2 c^4$ implies $\frac{dp}{dE} = \frac{E}{pc^2}$

the normalisation volume is just $\int d^3\mathbf{r} = \Omega$, and rotational invariance gives $d^3\mathbf{p} = 4\pi p^2 dp$.

All of which which simplifies the integral to

$$dn = \frac{\Omega^2}{4\pi^4 \hbar^6 c^6} E_e \sqrt{E_e^2 - m_e^2 c^4} E_\nu^2 \delta(E_e + E_\nu - E_0) dE_e dE_\nu$$

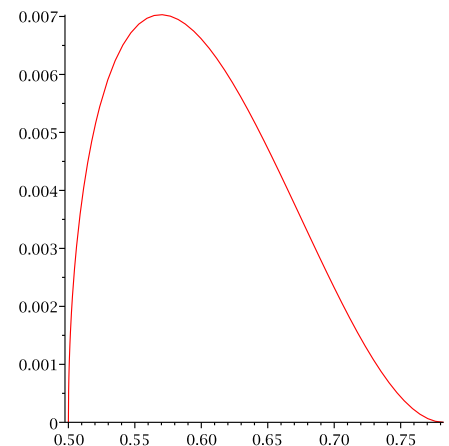
where E_e is the electron energy and E_ν is the neutrino energy. What can actually be measured is the electron energy, so we integrate over the neutrino energies,

$$\frac{dn}{dE_e} = \frac{\Omega^2}{4\pi^4 \hbar^6 c^6} E_e \sqrt{E_e^2 - m_e^2 c^4} (E_0 - E_e)^2$$

This is the distribution of electron energies from beta decay: the rate of emission of electrons at a particular energy is given by the Golden Rule

$$R = \frac{2\pi}{\hbar} \frac{G_F^2 M^2}{4\pi^4 \hbar^6 c^6} E_e \sqrt{E_e^2 - m_e^2 c^4} (E_0 - E_e)^2$$

Figure shows the simplest case of beta-emission: neutron decay. Conservation laws tell us that the electron energy must lie between its rest mass (0.51 MeV) and the total energy available (0.7823 MeV). But the entire shape can be deduced from geometry.



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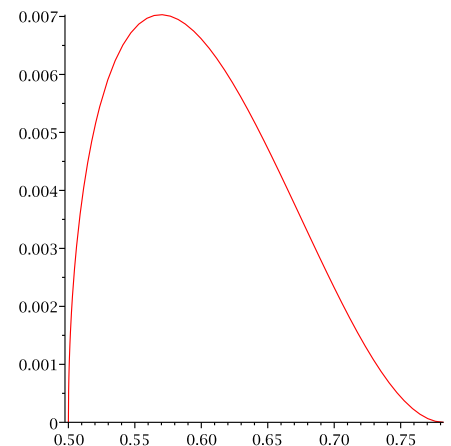
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6 Two state systems

6.1 Time Dependence

The exact expression for the time dependence of a system with N states required a set of N simultaneous differential equations. One case where we can solve this problem exactly is when we have a small number of states. Consider a system which requires only two basis states. Say we prepare it in initial state $|1\rangle$ and we want to know how long it will take to go to the other state $|2\rangle$. From section 5, we have two coupled equations in the time dependent c_1 and c_2 :

$$\begin{aligned}i\hbar\dot{c}_1 &= V_{11}c_1 + V_{12}c_2e^{i\omega_{12}t} \\i\hbar\dot{c}_2 &= V_{22}c_2 + V_{21}c_1e^{i\omega_{21}t}\end{aligned}$$

where $c_1(0) = 1$ and $c_2(0) = 0$.

If the change is slow, we can use first order time-dependent perturbation theory. We thus replace the $c_n(t)$ by $c_n(0)$, and integrate whence:

$$\begin{aligned}c_1 &\approx \exp(iV_{11}t/\hbar) \\|c_1|^2 &\approx 1 \\c_2 &\approx \frac{-i}{\hbar} \int_0^t V_{21}e^{i\omega_{21}t} dt\end{aligned}$$

Including the constant of integration for $c_1(0) = 1$.

6.2 Notes

- The ‘Matrix element’ V_{21} determines whether there is a transition from an initial state 1 to a final state 2 even if \hat{V} is *independent* of time. It also determines the rate of the transition.
- If the states $|1\rangle$ and $|2\rangle$ are eigenstates of the perturbation \hat{V} then $V_{21} = V_{12} = 0$ and no transition occurs.
- Over a long period of time, the system will oscillate between the two states.
- Perturbation theory, in essence, ignores the third-order possibility of ending up in state 2 via $|1\rangle \rightarrow |2\rangle \rightarrow |1\rangle \rightarrow |2\rangle$
- The mathematics is the same as for two coupled pendula, where the energy moves back and forth between the two bobs.
- The states can represent *anything*, and oscillation will occur whenever there are off diagonal terms in the matrix.
- Examples: (see Feynman III Ch.9-11) Nitrogen atom in ammonia, electron in H_2^+ , pion exchange, benzene, electron spins, photon polarisation, neutrino oscillations, neutral kaons.

6.3 Example: Oscillation in a fully mixing two state system

Consider the expectation value of a quantity S in a system which has two non-degenerate energy eigenstates $|1\rangle$ and $|2\rangle$, and where the Hermitian operator \hat{S} is defined by $\hat{S}|1\rangle = |2\rangle$, $\hat{S}|2\rangle = |1\rangle$.

The general state can be written:

$$|\phi\rangle = c_1 \exp(-iE_1 t/\hbar)|1\rangle + c_2 \exp(-iE_2 t/\hbar)|2\rangle$$

if we assume real c_1, c_2 it follows that the expectation value $\langle\hat{S}\rangle$ will be:

$$\begin{aligned}\langle\hat{S}\rangle &= \langle\phi|\hat{S}|\phi\rangle \\ &= [c_1 e^{iE_1 t/\hbar}\langle 1| + c_2 e^{iE_2 t/\hbar}\langle 2|] [c_1^* e^{-iE_1 t/\hbar}|2\rangle + c_2^* e^{-iE_2 t/\hbar}|1\rangle] \\ &= c_1 c_2 [e^{i\omega_{21} t} + e^{-i\omega_{21} t}] \\ &= 2c_1 c_2 \cos(\omega_{21} t)\end{aligned}$$

Thus the expectation value of \hat{S} oscillates in time at frequency $\omega_{21} = (E_2 - E_1)/\hbar$. This arises because \hat{S} is not compatible with the hamiltonian, and hence does not define a constant of the motion.

6.4 Neutrino Oscillations

Neutrino oscillation is a phenomenon where a specific flavour of neutrino (electron, muon or tau) is later measured to have different flavour. The probability of measuring a particular flavour varies periodically. The three neutrino states are created by a radioactive decay in a flavour eigenstate as $|f_1\rangle, |f_2\rangle, |f_3\rangle$ (electron, muon, tauon). However, these are not eigenstates of energy with a definite mass $|m_1\rangle, |m_2\rangle, |m_3\rangle$. We can expand the flavour eigenstate using the energy eigenstates as a basis:

$$|f_i\rangle = \sum_j \langle m_j | f_i \rangle |m_j\rangle$$

the energy eigenstates show how the wavefunctions behave in time, $m_j(t) = m_j(0) \exp(i\omega_j t)$, where $\omega_j = m_j c^2/\hbar$. $\omega_{ij} = (m_i - m_j)c^2/\hbar$. Consider an electron neutrino produced by a fusion reaction in the sun, $\Phi(t=0) = |f_1\rangle$, its wavefunction then varies as:

$$\Phi(t) = \sum_j |m_j\rangle \langle m_j | f_1 \rangle \exp(i\omega_j t)$$

For real neutrinos, the $\langle m_j | f_1 \rangle$ matrix has non-zero, possibly even complex elements everywhere, but here for simplicity we suppose that

$$\langle m_j | f_i \rangle = \begin{pmatrix} a & c & 0 \\ -c & a & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

with a and c real, time independent and $a^2 + c^2 = 1$ for normalisation. Our electron neutrino then evolves as $\Phi(t) = a \exp(i\omega_1 t)|m_1(t)\rangle + c \exp(i\omega_2 t)|m_2(t)\rangle$, so the probability that some time later it is still an electron neutrino is

$$\begin{aligned}|\langle f_1 | \Phi(t) \rangle|^2 &= |a^2 \exp(i\omega_1 t) + c^2 \exp(i\omega_2 t)|^2 \\ &= a^4 + c^4 + a^2 c^2 (\exp(i\omega_{21} t) + \exp(-i\omega_{21} t)) \\ &= 1 - 4a^2 c^2 \sin^2(\omega_{21} t/2)\end{aligned}$$

which is less than 1: it can somehow “turn into” a muon neutrino. Often, one writes $a = \sin \theta$ in which case $4a^2c^2 = \sin^2 \theta$. θ is referred to as a “mixing angle”.

If $a = c = \sqrt{\frac{1}{2}}$, then with a frequency governed by the difference in masses, the electron neutrino turns completely into a muon neutrino, then back again. With smaller c , there’s always some chance that it will still be an electron neutrino. In reality, it is also possible to oscillate into a tau neutrino. This underlies the “solar neutrino problem”. Detection of solar neutrinos was the subject of the 2002 Nobel prize. Similar oscillation occurs in the kaon system due to a symmetry-breaking effect called “CP violation” subject of the 2008 Nobel prize. Here one of the states is subject to radioactive decay, so a particle not only “turns into” something else, it also disappears when it does so!

6.5 Strong force - Two state system or degenerate perturbation

The fundamental forces can be thought of as manifestations of two state systems. Consider a system comprising a proton and a neutron. The proton can decay into a neutron plus a pion, while the neutron can absorb the pion and become a proton. We can think of the system as two neutrons and a pion: the pion having two degenerate states $|a\rangle$ and $|b\rangle$ depending on which neutron it is located. The off-diagonal terms are now $\langle a|\hat{V}_a|b\rangle$, where V_a is the potential energy of the pion due to neutron a . The two state analysis shows that we can think of the pion hopping back and forth between the neutrons (the pion exchange mechanism). Or we can treat the system by degenerate perturbation theory and diagonalise the 2x2 matrix to find energies: $V_{aa} \pm V_{ab}$. The ground state has a binding energy of $|V_{ab}|$

Note that V_{ab} involves the overlap between the state with the pion on one site and the state with the pion on the other site. Obviously this depends on the separation (R), and so there is a force between the neutrons dE_g/dR . As the nucleons move apart, the force depends on the tails of the wavefunctions, which in turn are exponentially dependent on the pion mass. Thus the strength of the strong force falls off exponentially with distance.

Note also that we have described the basis states of our two state system as ‘a proton and a neutron’, but the actual ground state is a mixture of the two. When interacting via the strong force, the nucleons lose their well-defined identity.

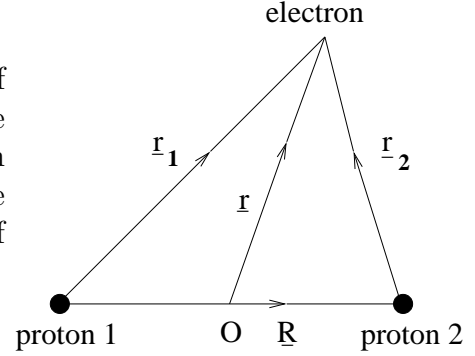
This picture of forces arising from exchange of ‘virtual’ particles (the pion is not observed as a free particle here) is the standard way of thinking about fundamental forces - the electromagnetic force involves ‘exchange of virtual photons’, the gravitational force ‘gravitons’ etc. These forces are long ranged (not exponentially decaying) because the particles involved have zero mass.

All of this is analogous to covalent bonding: ‘exchange of electrons’: and in each case there is still another level of understanding lurking beneath to define the potential V : QED (photons) for electron-ion bonding and QCD (gluons and quarks) for nucleon binding.

7 The H_2^+ Ion and Bonding

As the simplest example of covalent bonding, we consider the hydrogen molecular ion.

The hydrogen molecular ion H_2^+ is a system composed of two protons and a single electron. It is useful to use centre of mass (CM) coordinates by defining the relative position vector, \mathbf{R} , of proton 2 with respect to proton 1, and the position vector \mathbf{r} of the electron relative to the centre of mass of the two protons.



The Schrödinger equation is

$$\left[-\frac{\hbar^2}{2\mu_{12}} \nabla_R^2 - \frac{\hbar^2}{2\mu_e} \nabla_r^2 - \frac{e^2}{(4\pi\epsilon_0)r_1} - \frac{e^2}{(4\pi\epsilon_0)r_2} + \frac{e^2}{(4\pi\epsilon_0)R} \right] \psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R})$$

where the reduced mass of the two-proton system is $\mu_{12} = M/2$, with M the proton mass, and μ_e is the reduced mass of the electron/two-proton system:

$$\mu_e = \frac{m(2M)}{m + 2M} \simeq m$$

where m is the electron mass.

7.1 Born-Oppenheimer Approximation

Because nuclei are a great deal more massive than electrons, the motion of the nuclei is much slower than that of the electrons. Thus the nuclear and electronic motions can be treated more or less independently and it is a good approximation to determine the electronic states at any value of \mathbf{R} by treating the nuclei as fixed. This is the basis of the *Born-Oppenheimer approximation*.

In this approximation, the electron is described by an eigenfunction $U_j(\mathbf{r}, \mathbf{R})$ satisfying the Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu_e} \nabla_r^2 - \frac{e^2}{(4\pi\epsilon_0)r_1} - \frac{e^2}{(4\pi\epsilon_0)r_2} + \frac{e^2}{(4\pi\epsilon_0)R} \right] U_j(\mathbf{r}, \mathbf{R}) = E_j(\mathbf{R}) U_j(\mathbf{r}, \mathbf{R})$$

This is solved keeping \mathbf{R} constant. For each \mathbf{R} , a set of energy eigenvalues $E_j(\mathbf{R})$ and eigenfunctions $U_j(\mathbf{r}, \mathbf{R})$ is found. The functions $U_j(\mathbf{r}, \mathbf{R})$ are known as *molecular orbitals*.

The full wavefunction for the j^{th} energy level at given \mathbf{R} is taken to be the simple product

$$\psi(\mathbf{r}, \mathbf{R}) = F_j(\mathbf{R}) U_j(\mathbf{r}, \mathbf{R})$$

where $F_j(\mathbf{R})$ is a wavefunction describing the nuclear motion.

Substituting this form into the full Schrödinger equation and using the electronic equation yields

$$\left[-\frac{\hbar^2}{2\mu_{12}} \nabla_R^2 + E_j(\mathbf{R}) - E \right] F_j(\mathbf{R}) U_j(\mathbf{r}, \mathbf{R}) = 0$$

A little vector calculus gives

$$\begin{aligned} \nabla_R^2 \{F_j(\mathbf{R}) U_j(\mathbf{r}, \mathbf{R})\} &= \nabla_R \cdot \{ \nabla_R [F_j(\mathbf{R}) U_j(\mathbf{r}, \mathbf{R})] \} \\ &= \nabla_R \cdot \{ U_j(\mathbf{r}, \mathbf{R}) \nabla_R F_j(\mathbf{R}) + F_j(\mathbf{R}) \nabla_R U_j(\mathbf{r}, \mathbf{R}) \} \\ &= U_j(\mathbf{r}, \mathbf{R}) \nabla_R^2 F_j(\mathbf{R}) + F_j(\mathbf{R}) \nabla_R^2 U_j(\mathbf{r}, \mathbf{R}) \\ &\quad + 2 (\nabla_R U_j(\mathbf{r}, \mathbf{R})) \cdot (\nabla_R F_j(\mathbf{R})) \end{aligned}$$

Assuming that the variation of the molecular orbitals with inter-proton separation, \mathbf{R} , is weak, we can neglect the terms involving $\nabla_{\mathbf{R}} U_j(\mathbf{r}, \mathbf{R})$, and $\nabla_{\mathbf{R}}^2 U_j(\mathbf{r}, \mathbf{R})$ leaving a single-particle type Schrödinger equation for the nuclear motion

$$\left[-\frac{\hbar^2}{2\mu_{12}} \nabla_{\mathbf{R}}^2 + E_j(\mathbf{R}) - E \right] F_j(\mathbf{R}) = 0$$

in which $E_j(\mathbf{R})$ plays the role of a potential. We will return to this later.

7.2 The Electronic Ground State

We now try to investigate the lowest electronic levels of H_2^+ . First we look for symmetries, and note that, since $\mathbf{r}_1 = \mathbf{r} + \mathbf{R}/2$ and $\mathbf{r}_2 = \mathbf{r} - \mathbf{R}/2$, the electronic Hamiltonian is invariant under the parity operation $\mathbf{r} \rightarrow -\mathbf{r}$. If $\hat{\mathcal{P}}$ denotes the parity operator, then

$$[\hat{\mathcal{P}}, \hat{H}] = 0$$

These are commuting operators, so they can have the same eigenfunctions. These eigenfunctions are called *gerade* if the parity is even and *ungerade* if the parity is odd:

$$\hat{\mathcal{P}}U_j^g(\mathbf{r}, \mathbf{R}) = U_j^g(\mathbf{r}, \mathbf{R}), \quad \hat{\mathcal{P}}U_j^u(\mathbf{r}, \mathbf{R}) = -U_j^u(\mathbf{r}, \mathbf{R})$$

Now think about wave functions. If R is large, the system separates into a hydrogen atom and a proton (two degenerate states). The hydrogen atom has a large spacing between levels, so we use degenerate perturbation theory with $1s$ levels only. Quite generally, this procedure of taking linear combinations of atomic orbitals is known as the LCAO method. Note that this basis set is normalised, but neither complete nor orthogonal.

Since there must be solutions which are eigenfunctions of the parity operator, we take normalised linear combinations of gerade or ungerade symmetry of $1s$ orbitals:

$$\psi^g = [u_{1s}(r_1) + u_{1s}(r_2)]/\sqrt{2} \quad \text{and} \quad \psi^u = [u_{1s}(r_1) - u_{1s}(r_2)]/\sqrt{2}$$

We calculate the expectation value of the electronic Hamiltonian using these LCAO molecular wavefunctions:

$$E^{g,u}(\mathbf{R}) = \int \psi^{g,u*}(\mathbf{r}, \mathbf{R}) \hat{H} \psi^{g,u}(\mathbf{r}, \mathbf{R}) d^3r = \langle u_{1s}(r_1) | \hat{H} | u_{1s}(r_1) \rangle \pm \langle u_{1s}(r_1) | \hat{H} | u_{1s}(r_2) \rangle$$

where $+$ and $-$ correspond to u and g respectively, giving $E^g(\mathbf{R})$ and $E^u(\mathbf{R})$ for each value of \mathbf{R} ;

The evaluation of the integrals is complicated, but the results have the form:

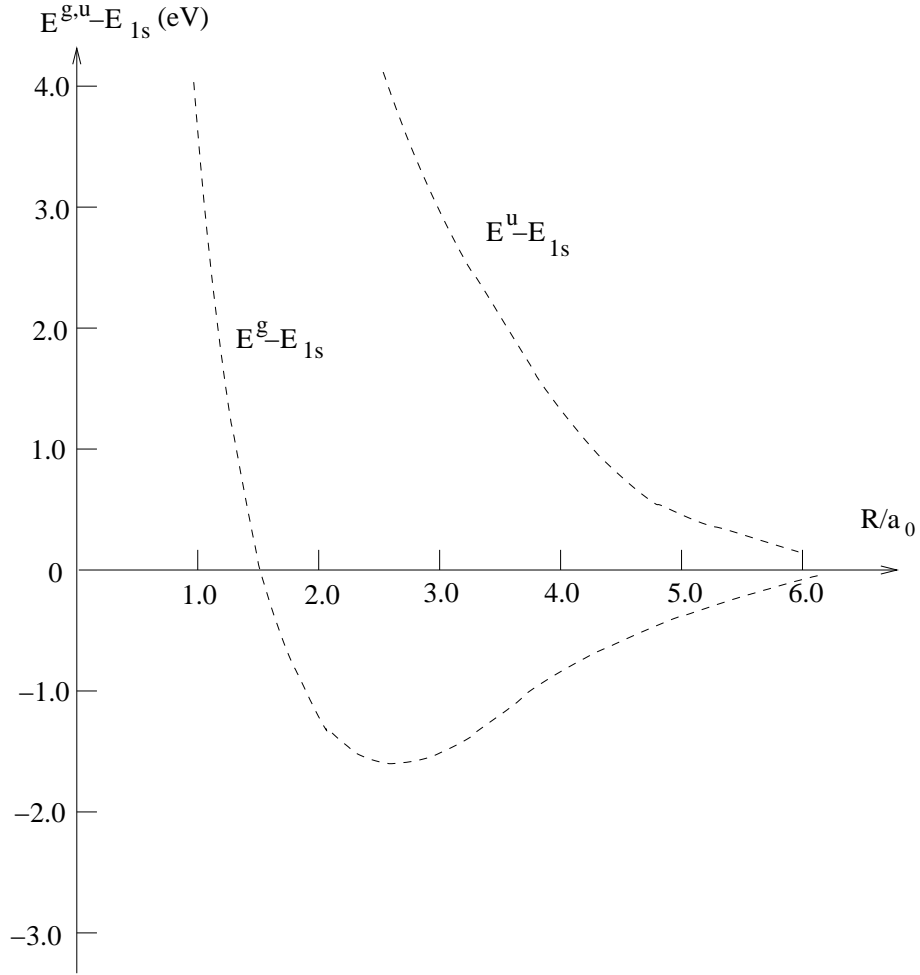
$$E^g(\mathbf{R}) = E_{1s} + \frac{e^2}{(4\pi\epsilon_0)R} \times \frac{(1 + R/a_0) \exp(-2R/a_0) + [1 - (2/3)(R/a_0)^2] \exp(-R/a_0)}{1 + [1 + (R/a_0) + (1/3)(R/a_0)^2] \exp(-R/a_0)}$$

and

$$E^u(\mathbf{R}) = E_{1s} + \frac{e^2}{(4\pi\epsilon_0)R} \times \frac{(1 + R/a_0) \exp(-2R/a_0) - [1 - (2/3)(R/a_0)^2] \exp(-R/a_0)}{1 - [1 + (R/a_0) + (1/3)(R/a_0)^2] \exp(-R/a_0)}$$

where a_0 is the Bohr radius and E_{1s} is the ground-state energy of atomic hydrogen.

The two curves $E^g - E_{1s}$ and $E^u - E_{1s}$ are plotted as a function of R . Note that the curve which corresponds to the symmetric (gerade) orbital exhibits a minimum at $R = R_0$, where $R_0/a_0 \simeq 2.5$, corresponding to $E^g - E_{1s} = -1.77$ eV. Since this is an upper bound on the ground-state energy, this implies that there is a stable bound state, a molecular ion. The curve represents an effective attraction between the two protons. By contrast, the curve corresponding to the ungerade orbital has no minimum, so that a H_2^+ ion in this state will dissociate into a proton and a hydrogen atom. If we think of the protons being attracted by the electron and repelled by each other, the symmetrical state should be the more tightly bound because the electron spends more of its time between the protons, where it attracts both of them. This is an example of *covalent* bonding.



7.3 Rotational and Vibrational Modes

We can now study the effective one-body Schrödinger equation for the nuclear motion by setting $E_j(\mathbf{R}) = E^g(R)$ for the ground state. Because $E^g(R)$ only depends on the magnitude of R it represents an effective central potential, so the solutions are of the form

$$F^g(\underline{R}) = \frac{1}{R} \mathcal{R}_{NL}(R) Y_{LM_l}(\theta, \phi)$$

where $Y_{LM_l}(\theta, \phi)$ are the spherical harmonics and the function $\mathcal{R}_{NL}(R)$ satisfies the radial equation

$$\left[-\frac{\hbar^2}{2\mu_{12}} \left(\frac{d^2}{dR^2} - \frac{L(L+1)}{R^2} \right) + E^g(R) - E \right] \mathcal{R}_{NL} = 0$$

We can approximate the centrifugal barrier term by setting it equal to its value at $R = R_0$, writing

$$E_r = \frac{\hbar^2}{2\mu_{12}R_0^2} L(L+1)$$

In this approximation we are treating the molecule as a rigid rotator. We can also approximate $E^g(R)$ by Taylor expanding about $R = R_0$. Because this point is a minimum, the first derivative is zero:

$$E^g(R) \simeq E^g(R_0) + \frac{1}{2}k(R - R_0)^2 + \dots$$

where k is the value of the second derivative of E^g at $R = R_0$.

With these two approximations, the radial equation becomes

$$\left[-\frac{\hbar^2}{2\mu_{12}} \frac{d^2}{dR^2} + \frac{1}{2}k(R - R_0)^2 - E_N \right] \mathcal{R}_{NL} = 0$$

where

$$E_N = E - E^g(R_0) - E_r$$

This is the equation for a simple harmonic oscillator with energies

$$E_N = \hbar\omega_0(N + \frac{1}{2}), \quad N = 0, 1, 2, \dots$$

where $\omega_0 = \sqrt{k/\mu_{12}}$. The vibrational energies are of the order of a few tenths of an eV, whereas the rotational energies are of the order of 10^{-3} eV. Both are much smaller than the spacing of the electronic levels. Transitions between these various levels give rise to *molecular spectra*. The pure rotational spectrum consists of closely-spaced lines in the infrared or microwave range. Transitions which also involve changes to the vibrational state give rise to *vibrational-rotational band spectra*.

7.4 Electronic states of the H_2 Molecule

Electrons are fermions with spin $\frac{1}{2}$, so the gerade state can be double occupied, as can the ungerade state (four states in all, same as two $1s$ orbitals for each ion). The second electron changes the structure of the wavefunction. Staying within LCAO, and ignoring spin, we can label basis states as, e.g. $u_{1s}^1(\mathbf{r}_2)$ indicating the first electron on the second atom. The electrons are indistinguishable, so the total wavefunctions (spin times spatial) must be eigenstates of parity and the *exchange* operator \hat{P}_{12} which switches the electron labels, e.g. $\hat{P}_{12}u_{1s}^1(\mathbf{r}_2) = u_{1s}^2(\mathbf{r}_2)$. They are fermions, hence antisymmetric: $P = -1$.

Assuming both electrons are $1s$ and in the bonding g state, and ignoring their interaction, the LCAO $1s^2$ spatial wavefunction is

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = [u_{100}^1(\mathbf{r}_1) + u_{100}^1(\mathbf{r}_2)][u_{100}^2(\mathbf{r}_1) + u_{100}^2(\mathbf{r}_2)]$$

This must be combined with a spin eigenfunction $\uparrow\uparrow, \downarrow\downarrow, (\uparrow\downarrow + \downarrow\uparrow)$, or $(\uparrow\downarrow - \downarrow\uparrow)$, where the first arrow represents the spin state ($m_s = \pm 1$) of the first electron. Since the spatial wavefunction is symmetric under label exchange, in fact it must be combined with the antisymmetric spin wavefunction $\uparrow\downarrow - \downarrow\uparrow$ to give the overall wavefunction in spin and space.

$$\psi(\mathbf{r}_1, \mathbf{r}_2, s_1, s_2) = [u_{100}^1(\mathbf{r}_1) + u_{100}^1(\mathbf{r}_2)][u_{100}^2(\mathbf{r}_1) + u_{100}^2(\mathbf{r}_2)][\uparrow\downarrow - \downarrow\uparrow]$$

This wavefunction describes two electrons, and is non-degenerate.

The second electron also adds an electron-electron repulsion to the Hamiltonian, which can be treated by perturbation theory.

$$\Delta E = \langle \psi(\mathbf{r}_1, \mathbf{r}_2) | e^2/4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2| | \psi(\mathbf{r}_1, \mathbf{r}_2) \rangle$$

There is a lot of subtlety here, since the electrons don't interact with themselves, only with each other, and we must avoid double-counting the interaction of 1-2 and 2-1. We'll return to this in more detail later in the context of Helium.

8 The Variational Principle

8.1 Approximate solution of the Schroedinger equation

If we can't find an analytic solution to the Schroedinger equation, a trick known as the variational principle allows us to estimate the energy of the ground state of a system. We choose an unnormalized trial function $\Phi(a_n)$ which depends on some *variational parameters*, a_n and minimise

$$E[a_n] = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

with respect to those parameters. This gives an approximation to the wavefunction whose accuracy depends on the number of parameters and the clever choice of $\Phi(a_n)$. For more rigorous treatments, a set of basis functions with expansion coefficients a_n may be used.

The proof is as follows, if we expand the normalised wavefunction

$$|\phi(a_n)\rangle = \Phi(a_n) / \langle \Phi(a_n) | \Phi(a_n) \rangle^{1/2}$$

in terms of the true (unknown) eigenbasis $|i\rangle$ of the Hamiltonian, then its energy is

$$E[a_n] = \sum_{ij} \langle \phi | i \rangle \langle i | \hat{H} | j \rangle \langle j | \phi \rangle = \sum_i |\langle \phi | i \rangle|^2 E_i = E_0 + \sum_i |\langle \phi | i \rangle|^2 (E_i - E_0) \geq E_0$$

where the true (unknown) ground state of the system is defined by $\hat{H}|i_0\rangle = E_0|i_0\rangle$. The inequality arises because both $|\langle \phi | i \rangle|^2$ and $(E_i - E_0)$ must be positive.

Thus the lower we can make the energy $E[a_i]$, the closer it will be to the actual ground state energy, and the closer $|\phi\rangle$ will be to $|i_0\rangle$.

If the trial wavefunction consists of a complete basis set of orthonormal functions $|\chi_i\rangle$, each multiplied by a_i : $|\phi\rangle = \sum_i a_i |\chi_i\rangle$ then the solution is exact and we just have the usual trick of expanding a wavefunction in a basis set. Alternately, we might just use an incomplete set with a few low-energy basis functions to get a $|\Phi\rangle$ close to the ground state $|i_0\rangle$. In practice, this is how most quantum mechanics problems are solved.

8.2 Excited States

The variational method can be adapted to give bounds on the energies of excited states, under certain conditions. Suppose we choose a trial function $\Phi_1(\beta_n)$ with variational parameters β_n . which is made orthogonal to the ground state ϕ_0 , by imposing the condition $\langle \phi_0 | \phi_1 \rangle = 0$.

If we know $|\phi_0\rangle = |i_0\rangle$, then similar to the above

$$E[a_n] = \frac{\langle \Phi_1 | \hat{H} | \Phi_1 \rangle}{\langle \Phi_1 | \Phi_1 \rangle} = \sum_{ij} \langle \phi_1 | i \rangle \langle i | \hat{H} | j \rangle \langle j | \phi_1 \rangle = \sum_i |\langle \phi_1 | i \rangle|^2 E_i = 0 + E_1 + \sum_{i=2} |\langle \phi_1 | i \rangle|^2 (E_i - E_1) \geq E_1$$

So the variational method gives an upper bound on the first excited-state energy, and so on. We can satisfy $\langle i_0 | \phi_1 \rangle = 0$ if $|i_0\rangle$ is known, *or* if it has a known symmetry from which we can exploit (e.g. if $|i_0\rangle$ has even parity, choosing $|\Phi_1\rangle$ to be odd.)

In general, though, we only have a variational estimate of the ground state $\phi_0(\alpha_n)$. In this case the expression above, subject to the constraint $\langle \phi_1(\beta_n) | \phi_0(\alpha_n) \rangle = 0$, gives an estimate of E_1 . However, the error in this approach will be larger than for E_0 because not only is the wavefunction incorrect, but also the constraint $\langle \phi_1 | \phi_0 \rangle = 0$ is not quite correct; using an approximate ground state does not guarantee that we get an upper bound for the excited states.

If the excited state has different symmetry from those of the lower-lying levels, and we choose trial functions with the correct symmetries, orthogonality is guaranteed and we get an upper bound to the energy of the lowest-lying level with those symmetries, which is the excited state.

8.3 Analytic example of variational method - Binding of the deuteron

Say we want to solve the problem of a particle in a potential $V(r) = -Ae^{-r/a}$. This is a model for the binding energy of a deuteron due to the strong nuclear force, with $A=32\text{MeV}$ and $a=2.2\text{fm}$. The strong nuclear force does not exactly have the form $V(r) = -Ae^{-r/a}$, unlike the Coulomb interaction we don't know what the exact form should be, but $V(r) = -Ae^{-r/a}$ is a reasonable model.

The potential is spherically symmetric, most attractive at $r = 0$ and falls rapidly to zero at large r , so we choose a trial wavefunction which does the same, say $\phi = ce^{-\alpha r/2a}$. This has only one dimensionless variational parameter, α . The value of c follows from normalisation $\int c^2 e^{-\alpha r/a} 4\pi r^2 dr = 1$; which gives $c^2 = \alpha^3/8\pi a^3$. (The $4\pi r^2$ comes from the problem being three dimensional).

According to the variational principle, our best estimate for the ground state using this trial function comes from minimising $\langle \phi | \hat{H} | \phi \rangle$ with respect to α .

$$\begin{aligned} \langle \phi | H | \phi \rangle / \langle \phi | \phi \rangle &= \frac{-\hbar^2}{2m} \int_0^\infty c^2 \left(e^{-\alpha r/2a} \nabla^2 e^{-\alpha r/2a} \right) 4\pi r^2 dr - A \int_0^\infty c^2 \exp[-(\alpha + 1)r/a] 4\pi r^2 dr \\ &= \frac{\hbar^2 \alpha^2}{8ma^2} - A \left(\frac{\alpha}{\alpha + 1} \right)^3 \end{aligned}$$

From this we find the minimum for $E(\alpha)$ at α_0

$$\frac{dE}{d\alpha} = \frac{\hbar^2 \alpha}{4ma^2} - 3A \left(\frac{\alpha^2}{(\alpha + 1)^4} \right) = 0 \quad \Rightarrow \quad \frac{(\alpha_0 + 1)^4}{\alpha_0} = 12Ama^2/\hbar^2$$

Solving for α_0 gives $\alpha_0 = 1.34$, and substituting back into $\langle \phi | H | \phi \rangle$ gives $E_0 = -2.14\text{MeV}$.

This is fairly close to the exact solution for this potential, which can be obtained analytically as a Bessel function of $\sqrt{8mA}(a/\hbar)e^{-r/2a}$ if you manage to spot that change of variables! The exact solution gives $E_0 = -2.245\text{MeV}$.

8.4 Quantum forces: the Hellmann-Feynman Theorem

For many systems one is often interested in *forces* as well as energies. If we can write the energy of a in state ϕ as $E = \langle \phi | \hat{H} | \phi \rangle$ and differentiate with respect to some quantity α then

$$\frac{dE}{d\alpha} = \left\langle \frac{d\phi}{d\alpha} | \hat{H} | \phi \right\rangle + \langle \phi | \frac{d\hat{H}}{d\alpha} | \phi \rangle + \langle \phi | \hat{H} | \frac{d\phi}{d\alpha} \rangle$$

But since $\hat{H}|\phi\rangle = E|\phi\rangle$ and $\langle \phi | \phi \rangle$ is 1 for normalisation:

$$\frac{dE}{d\alpha} = \langle \phi | \frac{d\hat{H}}{d\alpha} | \phi \rangle + E \frac{d}{d\alpha} \langle \phi | \phi \rangle = \langle \phi | \frac{d\hat{H}}{d\alpha} | \phi \rangle$$

This result is called the Hellmann-Feynman theorem: the first differential of the expectation value of the Hamiltonian with respect to *any quantity* does not involve differentials of the wavefunction.

e.g. if α represents the position of a nucleus in a solid, then the force on that nucleus is the expectation value of the force operator $\frac{d\hat{H}}{d\alpha}$. It can be applied to any quantity which is a differential of the Hamiltonian provided the basis set does not change.

Caveat: if we use an incomplete basis set which depends explicitly the positions of the atoms, then we have $|\phi\rangle = \sum_{n,i} |u_{n,i}(\mathbf{r})\rangle$. This give spurious so-called ‘‘Pulay’’ forces if ϕ is not an exact eigenstate.

8.5 An aside about Kinetic Energy

The expectation value of the kinetic energy $\langle \hat{T} \rangle$ is always positive. This can be shown by an integration by parts in which the first term vanishes provided the wavefunction tends to zero at infinity (which it will for a bound state). In 1D:

$$\langle \hat{T} \rangle = \frac{-\hbar^2}{2m} \int \Phi^* \frac{d^2}{dx^2} \Phi dx = \frac{-\hbar^2}{2m} [\Phi^* \frac{d}{dx} \Phi]_{-\infty}^{\infty} + \frac{\hbar^2}{2m} \int \frac{d}{dx} \Phi^* \frac{d}{dx} \Phi dx = \frac{\hbar^2}{2m} \int \left| \frac{d}{dx} \Phi \right|^2 dx$$

The second term integrand is positive everywhere, so the kinetic energy is always positive.

8.6 Variational Method in MAPLE

The variational method is exceptionally well suited to computer algebra packages such as maple. The procedure is as follows:

- Define Trial wavefunction Φ
- Evaluate Normalization factor $|c^2| = \langle \Phi | \Phi \rangle$
- Evaluate unnormalised kinetic energy $\langle T \rangle = -\hbar^2 \langle \Phi | \nabla^2 | \Phi \rangle / 2m$
- Evaluate unnormalised potential energy $\langle V \rangle = \langle \Phi | \hat{V} | \Phi \rangle$
- Differentiate with respect to variational parameters $D_{a_n} = \frac{d}{da_n} (\langle T \rangle + \langle V \rangle) / c^2$
- Solve $D_{a_n} = 0$ for all a_n
- Substitute optimal value for a_n into Φ .
- Evaluate $[\langle T \rangle + \langle V \rangle] / c^2$ using optimised wavefunction.

If one needs to do another variational calculation for a different potential and trial wavefunction, only definitions 1 and 3 need to be changed.

8.7 Density functional theory (Nobel prize 1998)

If we consider the total probability density of a system of many interacting particles $\rho(\mathbf{r})$, there may be several possible wavefunctions which could give rise to it: call this set $S(\Phi)$.

Now, consider the expectation value of the energy $\langle \hat{H} \rangle$. We know from the variational principle that $\langle \hat{H} \rangle \geq E_o$. If we define a functional $F[\rho(\mathbf{r})] = \text{Min}_{S(\Phi)} \langle \hat{H} \rangle$, then it follows that $F[\rho] \geq E_o$.

Consequently we can use the variational principle to find the $\rho(\mathbf{r})$ which minimises the value of F , and this may give us the ground state energy *without having to evaluate the wavefunction*. This is especially useful when the wavefunction consists of complex combinations of many different single-particle wavefunctions, as with the many electrons in a solid or molecule.

The drawback is that for interacting electrons, the functional is not known.

8.8 Kohn-Sham functional

For solids, we have 10^{26} electron states. Analytic solution becomes impossible. In the past 20 years the density functional theory has come to dominate condensed matter physics, extending to chemistry, materials, minerals and beyond.

A popular form of DFT functional was introduced by Nobel laureate Walter Kohn and Lu Sham:

$$F(\rho) = T[\rho] + \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}d^3\mathbf{r}' + E_{xc}[\rho] + \sum_i \int \frac{Z_i e \rho(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{R}_i - \mathbf{r}'|} d^3\mathbf{r}'$$

Nobody has found a satisfactory functional for T . What is generally used is:

$$-\frac{\hbar^2}{2m} \sum_i \int \phi_i \nabla_i^2 \phi_i d^3\mathbf{r}$$

which is the kinetic energy of non-interacting “quasiparticles” and depends explicitly on the wavefunctions. The integrals represent electrostatic interactions between the electrons and between electrons and ions, and E_{xc} is ‘everything else’. The advantage of this form is that it can be recast to give a set of one-particle equations with non-interacting fermions moving in an effective potential:

$$V_{eff} = \sum_{ion} \frac{Ze}{4\pi\epsilon_0|\mathbf{R}_{ion} - \mathbf{r}'|} + \int \frac{\rho(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}$$

Since V_{eff} depends on $\rho(\mathbf{r})$ these equations must be solved self-consistently.

Thus the density functional theorem shows that the problem of solving the Schroedinger equation for a collection of interacting electrons can be transformed to that of a system of non-interacting ‘quasiparticles’, with the cost that the Hamiltonian depends on the electron density $\rho(\mathbf{r})$:

$$H[\rho(\mathbf{r})]\phi_i = E_i\phi_i \quad \text{where} \quad \rho(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2$$

Thus the Schroedinger equation is a nonlinear differential equation of many variables. Thus we must turn to the variational method. The most general approach here is to use a Fourier Series (plane wave basis set). The wavefunction for the i th electron is then written as

$$\phi_i = \sum_k c_{ik} \exp(-i\mathbf{k} \cdot \mathbf{r}) \quad \text{and the variational equation becomes:} \quad E_0 = \text{Min} \sum_i \langle \phi_i | \hat{H}(\rho) | \phi_i \rangle$$

The accuracy of the ground state energy of the electrons is determined by the number of Fourier components used. The wavefunctions are expanded in a computer-friendly basis set and the variational principle is used to transform the problem from a set coupled non-linear differential equations into a minimisation of a single function of many variables. Most structural properties of materials depend only on the electron ground state.

The single particle eigenstates of Kohn-Sham functional are not proper single electron states: indistinguishability means there is no such thing. Nevertheless, they are Bloch states, and they do exhibit well defined symmetry and energy “band-structure” which can help with interpretation of the electronic structure

9 Indistinguishable Particles and Exchange

Quantum mechanics allows us to predict the results of experiments. If we conduct an experiment with indistinguishable particles a correct quantum description cannot allow anything which distinguishes between them. For example, if the wavefunctions of two particles overlap, and we detect a particle, which one is it? The answer to this is not only that we don't know, but that we can't know. Quantum mechanics can only tell us the probability of finding *a* particle in a given region. The wavefunction must therefore describe *both* particles. The Schroedinger equation is then:

$$\left[-\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + V(\mathbf{r}_1) + V(\mathbf{r}_2) \right] \Phi(\mathbf{r}_1, \mathbf{r}_2) = E\Phi(\mathbf{r}_1, \mathbf{r}_2)$$

where the subscripts label each particle, and there are six coordinates, three for each particle. Φ is a wave in six dimensions which contains the information we can measure: the probability of finding particles at \mathbf{r}_1 and \mathbf{r}_2 , but *not* what we can't measure: which particle is which.

What basis states would be appropriate for Φ ? An *approximation* is to use a product such as $\Phi(\mathbf{r}_1, \mathbf{r}_2) = |a(\mathbf{r}_1)b(\mathbf{r}_2)\rangle$ where $a(\mathbf{r}_1)$ and $b(\mathbf{r}_2)$ are one-particle wavefunctions of atoms 1 and 2. This allows us to separate the two particle equation into two one particle equations:

$$\left[\frac{-\hbar^2}{2m}\nabla_1^2 + V(r_1) \right] |a(\mathbf{r}_1)\rangle = E_1 |a(\mathbf{r}_1)\rangle; \quad \left[\frac{-\hbar^2}{2m}\nabla_2^2 + V(r_2) \right] |b(\mathbf{r}_2)\rangle = E_2 |b(\mathbf{r}_2)\rangle$$

provided that the particles do not interact (n.b ∇_1^2 does not act on $b(\mathbf{r}_2)$).

Unfortunately, by doing this we have introduced unphysical *labels* to the indistinguishable particles. And this is wrong: the effect of it is that the particles do not interfere with each other because they are in different dimensions (six dimensional space - remember?). When we construct a two-particle wavefunction out of two one-particle wavefunctions we must ensure that the probability density (the *measurable* quantity $|\Phi|^2$) is independent of the *artificial* labels.

9.1 The exchange operator and Pauli's exclusion principle

We introduce the *exchange operator* \hat{P}_{12} : an operator which permutes the labels of the particles. This is a rather strange operator, because it only changes the *unphysical* labels which we have attached to the one-particle wavefunctions in order to make the maths more easy. For a meaningful solution we must have a wavefunction which has a probability amplitude unchanged by \hat{P}_{12} : it must be symmetric or antisymmetric with respect to exchange: $|\Phi(\mathbf{r}_1, \mathbf{r}_2)\rangle = \pm |\Phi(\mathbf{r}_2, \mathbf{r}_1)\rangle$.

Physical solutions must be eigenfunctions of \hat{P}_{12} with eigenvalues $+1$ (bosons) or -1 (fermions). Also, any physically meaningful Hamiltonian must commute with \hat{P}_{12} , otherwise \hat{H} and \hat{P}_{12} could not have common eigenfunctions and the system could not remain in an eigenstate of exchange.

A simple product wavefunction $|a(\mathbf{r}_1)b(\mathbf{r}_2)\rangle$ does not satisfy this (unless $a = b$). A linear combination of all permutations is required, for two particles:

$$|\Phi^-\rangle = |a(\mathbf{r}_1)b(\mathbf{r}_2) - a(\mathbf{r}_2)b(\mathbf{r}_1)\rangle / \sqrt{2}$$

$$|\Phi^+\rangle = C_{ab}|a(\mathbf{r}_1)b(\mathbf{r}_2) + a(\mathbf{r}_2)b(\mathbf{r}_1)\rangle + C_{aa}|a(\mathbf{r}_2)a(\mathbf{r}_1)\rangle + C_{bb}|b(\mathbf{r}_2)b(\mathbf{r}_1)\rangle$$

where the C_{ab} terms are expansion and normalisation parameters. Note that the antisymmetric combination cannot include terms where both particles are in the same state, but there are three possibilities for the symmetric state. Although any linear combinations of C_{ab} C_{bb} and $C_{aa} = 1$ are possible, C_{bb} and C_{aa} correspond to different configurations and are usually set to zero.

Notice that if $a = b$, then $|\Phi^-\rangle = 0$. Thus there is no possible antisymmetric combination involving identical states, i.e. two fermions cannot be in the same quantum state: the Pauli exclusion principle.

9.2 Two indistinguishable particles with spin 1/2

If we have two identical fermions of spin 1/2, confined in the same region, what is the appropriate wavefunction? In the scattering case we could measure spins far from the interaction, and if we knew that the total spins is conserved, spins can be associated with each particle. In the bound state we cannot tell which particle we are measuring, so the ket must contain both spin and spatial wavefunctions of both particles.

Assuming the spins do not interact, we can separate the two-particle spin wavefunction into $\sigma(1,2) = \sigma_1\sigma_2$. We also know the appropriate one particle basis states $\uparrow_1, \downarrow_1, \uparrow_2, \downarrow_2$, where \uparrow_1 represents “particle 1” in spinor state $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$. The combinations for indistinguishable particles are then:

$$\uparrow_1\uparrow_2, \quad \downarrow_1\downarrow_2, \quad (\uparrow_1\downarrow_2 + \downarrow_1\uparrow_2)/\sqrt{2}, \quad (\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2)/\sqrt{2}$$

Operating on these with \hat{P}_{12} yields eigenvalues 1, 1, 1 and -1 respectively. $\mathbf{S}^2 = S(S+1)$ yields 2, 2, 2 and 0, S_z yields 1,-1,0 and 0. Thus the demands of indistinguishability couples the spins of two identical particles into a triplet ($S=1$) and a singlet ($S=0$). The spin-1 vector has three possible M_s component values - hence the triplet.

9.3 The exchange interaction

The *overall* wavefunction describing fermions must be antisymmetric with respect to exchange, i.e. $\hat{P}_{12}|\Phi\rangle = -|\Phi\rangle$. Therefore in an atom or molecule where Φ includes both spin and spatial parts, the spin and spatial parts of a fermionic wavefunction have opposite exchange symmetry.

Spin must be considered even if the energy (Coulomb potential) depends explicitly only on the spatial part. The expectation value of the potential energy is different for symmetric and anti-symmetric spatial combinations. Using $|\Phi^\pm\rangle$ from above (with $C_{ab} = 1$).

$$\langle\Phi^\pm|\hat{V}|\Phi^\pm\rangle = \langle a(\mathbf{r}_1)b(\mathbf{r}_2)|V(r)|a(\mathbf{r}_1)b(\mathbf{r}_2)\rangle \pm \langle a(\mathbf{r}_1)b(\mathbf{r}_2)|V(r)|a(\mathbf{r}_2)b(\mathbf{r}_1)\rangle$$

The first term is called the direct interaction and the second term is known as the exchange interaction: a measurable contribution to the energy comparable in size to the first, which has no classical analogue.

9.4 Spins and Exchange

Now notice something strange. The exchange interaction has split the $\mathbf{S}=1$ states from the $\mathbf{S}=0$ states. We could write the potential as $\hat{V} = J_{nl} - (2\hat{\mathbf{S}} - 1)K_{nl}$, even though the Hamiltonian does not act on the spin! This is because the sign of the exchange integral depends on the (anti)symmetry of the spatial wavefunction. Thus we can write the matrix element as

$$\langle\Phi|J_{nl} - (2S - 1)K_{nl}|\Phi\rangle$$

This ‘exchange interaction’ appears to depend on the spin - the triplet states have lower energy than the singlet (this is one of *Hund’s rules* for determining energy levels in atoms). It is this type of exchange force which keeps spins aligned in a ferromagnet, not the magnetic interaction itself.

9.5 Wavefunction for many spin one-half particles

The exchange arguments for two-particle systems can be extended to many particle systems: The indistinguishable wavefunction consists of all possible permutations of the product of one electron wavefunctions. For the symmetric case $\hat{P}_{nm}\Phi = \Phi$, a product of these permutations will suffice. For the antisymmetric case, the correct form turns out to be given by the determinant of a matrix:

$$\Phi = \frac{1}{\sqrt{N!}} \det \begin{pmatrix} \phi_a(1) & \phi_b(1) & \dots & \phi_N(1) \\ \phi_a(2) & \phi_b(2) & \dots & \phi_N(2) \\ \dots & \dots & \dots & \dots \\ \phi_a(N) & \phi_b(N) & \dots & \phi_N(N) \end{pmatrix}$$

This is called a *Slater Determinant*. For fermions, where $\hat{P}_{nm}\Phi = -\Phi$ the Slater Determinant obeys the Pauli exclusion principle: if any two of the one-particle wavefunctions were identical ($\phi_n = \phi_m$), then the wavefunction would be the determinant of a matrix with two identical rows, i.e. zero.

Note also that $\langle \Phi | \hat{H} | \Phi \rangle$ has many more exchange terms than direct ones.

9.6 Helium

Helium is the simplest system for which we are unable to accurately calculate the energy.

For a single electron moving in the field of a helium nucleus, the spatial wavefunctions are similar to those of hydrogen $|u_{nlm}\rangle$.

When a second electron is added, a reasonable basis set is exchange-symmetrised wavefunctions consisting of spin states multiplying hydrogenic spatial parts:

$$(u_{nlm}(\mathbf{r}_1)u_{n'l'm'}(\mathbf{r}_2) \pm u_{n'l'm'}(\mathbf{r}_1)u_{nlm}(\mathbf{r}_2))$$

Since the overall wavefunction must be antisymmetric, the singlet (exchange-antisymmetric) spin states must combine with symmetric spatial states, and the triplet (exchange-symmetric) spin states must combine with antisymmetric spatial states.

If both electrons were in the same spatial state, the antisymmetric spatial wavefunction would be:

$$|(a(\mathbf{r}_1)a(\mathbf{r}_2) - a(\mathbf{r}_2)a(\mathbf{r}_1))\rangle = 0$$

Hence there is no triplet for the ground state.

9.7 Electron-electron interaction - ground state by perturbation theory

The hydrogen wavefunctions are only a choice of basis set: the hydrogenic potential ignores the electron-electron repulsion. A simple approach is to treat this as a perturbation and to use degenerate perturbation theory.

The perturbing potential is just $V = e^2/4\pi\epsilon_0 r_{12}$ where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. The unperturbed spatial ground state is just a product of the hydrogenic ones with $Z=2$ for helium:

$$u_{100}(r_1)u_{100}(r_2) = \frac{Z^3}{\pi a_0^3} e^{-Zr_1/a_0} e^{-Zr_2/a_0}$$

so by perturbation theory, the energy shift due to this potential is given by:

$$\langle u_{100}(r_1)u_{100}(r_2) | e^2/4\pi\epsilon_0 r_{12} | u_{100}(r_1)u_{100}(r_2) \rangle$$

The electron-electron repulsion is over 30% of the unperturbed energy ($4Z\mu e^4/\hbar^2$), so perturbation theory may seem inappropriate. Strictly, it isn't even the right integral, as it neglects correlation. But in fact the value of this integral is $5Z\mu e^4/8\hbar^2$ within 5% of the actual energy.

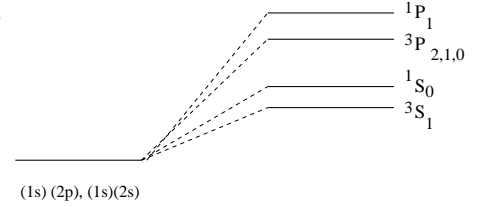
Note also that the radial wavefunctions are different for 2s and 2p, so the electron-electron interaction splits the degeneracy between 1s2s and 1s2p configurations.

9.8 Multiplicity and Degeneracy of Excited States

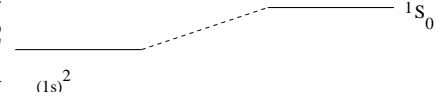
Ignoring electron-electron interaction, all 1s2s and 1s2p states have the same energy. The perturbation ($e^2/4\pi\epsilon_0 r_{12}$) lifts that degeneracy, and we can treat it with degenerate perturbation theory. Rather than evaluating the integral in the 4x4 matrix exactly, we can use a physical argument: ($e^2/4\pi\epsilon_0 r_{12}$) is not an external potential, and so applies no net torque or force on the electrons. The perturbation cannot change the angular momentum, so it cannot mix states with different l or m . The theta integral will be $\delta_{ll'}$, and the phi integral $\delta_{mm'}$, total angular momentum remains a good quantum number: $L=0(1s2s)$ or $L=1(1s2p)$. Since the 2s state has finite probability of being at the nucleus, and the 2p has zero probability of being there, the 2s state is less well *screened* from the nuclear charge by the 1s and will have lower energy.

For a given spatial excited state the possible normalised spin wavefunction combinations, consistent with the anti-symmetry requirement are a spin triplet and a spin singlet.

$$\begin{aligned}\Phi_3 &= (\phi_{nlm,n'l'm'} - \phi_{n'l'm',nlm})(\uparrow\uparrow)/\sqrt{2} \\ &= (\phi_{nlm,n'l'm'} - \phi_{n'l'm',nlm})(\downarrow\downarrow)/\sqrt{2} \\ &= (\phi_{nlm,n'l'm'} - \phi_{n'l'm',nlm})(\uparrow\downarrow + \downarrow\uparrow)/2 \\ \Phi_1 &= (\phi_{nlm,n'l'm'} + \phi_{n'l'm',nlm})(\uparrow\downarrow - \downarrow\uparrow)/2\end{aligned}$$



Where $|\phi_{nlm,n'l'm'}\rangle$ represents electron 1 in a hydrogenic state with quantum numbers n, l and m and electron 2 with n', l' , and m' . The subscripts on the Φ label spin *multiplicity* ($2S+1$)



Again whole effect of the potential is contained in the spatial part, the spin integral will be $\delta_{\sigma\sigma'}$. so off-diagonal matrix elements are all zero. We need to evaluate

$J_{nl} = \langle \phi_{nlm,n'l'm'} | (e^2/4\pi\epsilon_0 r_{12}) | \phi_{nlm,n'l'm'} \rangle$ - the *direct* integral.

$K_{nl} = \langle \phi_{nlm,n'l'm'} | (e^2/4\pi\epsilon_0 r_{12}) | \phi_{n'l'm',nlm} \rangle$ - the *exchange* integral.

with which perturbation theory gives an energy shift in the $1s^1 2s^1$ state of:

$$\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} (\langle \phi_{100,200} | 1/r_{12} | \phi_{100,200} \rangle + \langle \phi_{200,100} | 1/r_{12} | \phi_{200,100} \rangle \pm \langle \phi_{100,200} | 1/r_{12} | \phi_{200,100} \rangle \pm \langle \phi_{200,100} | 1/r_{12} | \phi_{100,200} \rangle)$$

where the + applies to the singlet state and the - to the triplet. The direct integral, electron-electron repulsion, increases the energy, but the exchange integral can either increase or decrease energy.

Thus the energy levels are split by different direct interactions into $L=0$ and $L=1$ and again through exchange interaction into singlet and triplet. The final degeneracies of states with one electron excited to $n=2$ are 3,1,9 and 3. The spectroscopic notation in the figure gives the quantum numbers as: $(nl)(n'l')^{2S+1}L_J$

Again, the most useful quantum number labels are the total spin and angular momentum: we could write the perturbation energy as $\Delta E = J_{nl} - (2S - 1)K_{nl}$, even though the perturbing potential does not act on the spin. The 'exchange force' selects preferred spin state via the requirement of overall antisymmetry.

10 Self-consistent field theory

An important unsolved problem in quantum mechanics is how to deal with indistinguishable, interacting particles - in particular electrons which determine the behaviour of almost every object in nature. The basic problem is that if particles interact, that interaction must be in the Hamiltonian. So until we know where the particles are, we can't write down the Hamiltonian, but until we know the Hamiltonian, we can't tell where the particles are.

10.1 Hartree-Fock theory

The idea is to solve the Schroedinger equation for an electron moving in the potential of the nucleus and all the other electrons. We start with a guess for the trial electron charge density, solve $Z/2$ one-particle Schroedinger equations (initially identical) to obtain Z electron wavefunctions. Then we construct the potential for each wavefunction from that of the nucleus and that of all the other electrons, symmetrise it, and solve the $Z/2$ Schroedinger equations again.

Fock improved on Hartree's method by using the properly antisymmetrised wavefunction (Slater determinant) instead of simple one-electron wavefunctions. Without this, the exchange interaction is missing. This method is ideal for a computer, because it is easily written as an algorithm.

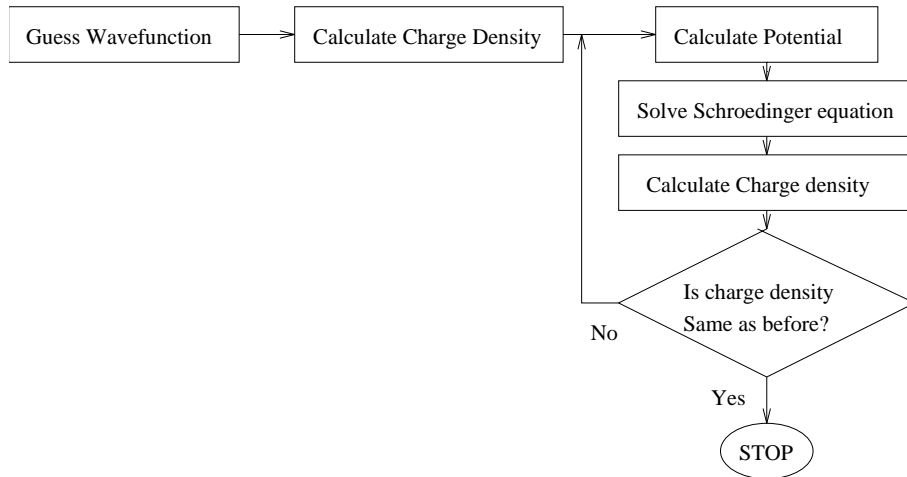


Figure 5: Algorithm for Self-consistent field theory.

Although we are concerned here with atoms, the same methodology is used for molecules or even solids (with appropriate potential symmetries and boundary conditions). This is a variational method, so wherever we refer to wavefunctions, we assume that they are expanded in some appropriate basis set.

The full set of equations are

$$\epsilon_i \psi_i(\mathbf{r}) = \left(-\frac{1}{2} \nabla^2 + V_{ion}(\mathbf{r}) \right) \psi_i(\mathbf{r}) + \sum_j \int d\mathbf{r}' \frac{|\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r}) - \sum_j \delta_{\sigma_i \sigma_j} \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \psi_j(\mathbf{r}) \quad (3)$$

The first term is the kinetic energy and electron-ion potential. The second ‘Hartree’ term, is the electrostatic potential from the charge distribution of N electrons, including an unphysical self-interaction of electrons when $j = i$. The third, ‘exchange’ term, acts only on electrons with the same spin and comes from the Slater determinant form of the wavefunction.

Physically, the effect of exchange is for like-spin electrons to avoid each other. Each electron is surrounded by an ‘exchange hole’: there is one fewer like-spin electrons nearby than the mean-field would imply. The term $i = j$ neatly cancels out the self interaction of the electron.

10.2 Self-consistent fields

Iterative, self-consistent approaches similar to the Hartree-Fock method can be used to calculate properties of atoms, solids or molecules. All that changes is V_{ion} .

For non-central potentials appropriate boundary conditions are needed (e.g. periodic in the case of crystals). One of the main problems now is to select an appropriate basis set for the problem. Various options exist: Plane waves, atomic orbitals, ‘augmented’ plane waves which wiggle more near to the nuclei, gaussian or ‘muffin tin’ orbitals which are localised on the nuclei. There is still a huge amount of research going on in this area.

10.3 Correlation: conditional probability

Hartree-Fock theory does not properly describe correlation. In the Copenhagen Interpretation, the squared modulus of the wavefunction gives the probability of finding a particle in a given place. The many-body wave function gives the N-particle distribution function, i.e. $|\Phi(r_1, \dots, r_N)|^2$ is the probability density that particle 1 is at \mathbf{r}_1 , ..., and particle N is at \mathbf{r}_N .

But when trying to work out the interaction between electrons, what we want to know is the probability of finding an electron at \mathbf{r} , *given the positions of all the other electrons* $\{\mathbf{r}_i\}$. This implies that the electron behaves quantum mechanically when we evaluate its wavefunction, but as a classical point particle when it contributes to the potential seen by the other electrons.

10.4 Lattice methods: Variational method by computer

The variational method transposes the problem of solving a differential equation onto the problem of minimising a function of many variables. It is therefore good for use with computers.

One of the simplest ways of solving for the ground state of a system with a computer is to use a basis set consisting of the values of $|\phi\rangle$ defined on a lattice. In 1D such a solution is simply a histogram where we adjust the wavefunction at each point until the energy of the whole system is minimised. The kinetic energy (second derivative of the wavefunction) must then be obtained by some interpolation method. The weights of $|\phi\rangle$ at each point can be regarded as a basis set. It is not complete, but it becomes more and more complete as the lattice gets finer.

Another common way of solving the Schroedinger equation numerically is to write the wavefunction as a Fourier series.

$$\Phi(\mathbf{b}) = \sum_{\mathbf{b}} a_{\mathbf{b}} e^{i\mathbf{b} \cdot \mathbf{r}}$$

where $a_{\mathbf{b}}$ are the variational parameters. Using Fourier series (also called plane wave expansions) has several advantages. Increasing accuracy can be obtained by adding more Fourier components (because each plane wave is orthogonal to all the others), the value of $\Phi(\mathbf{r})$ can be quickly found by a Fourier transform of $a(\mathbf{k})$ and the kinetic energy has particularly simple form because

$$\frac{-\hbar^2}{2m} \frac{\int \Phi^* \nabla^2 \Phi d^3\mathbf{r}}{\int \Phi^* \Phi d^3\mathbf{r}} = \frac{\sum_{\mathbf{b}} a_{\mathbf{b}}^2 \frac{\hbar^2 b^2}{2m}}{\sum_{\mathbf{b}} a_{\mathbf{b}}^2}$$

which requires no numerical differentiation if used on a computer. The wavefunctions must be normalised, e.g. with Periodic Boundary Conditions. For a periodically repeating crystal, these are exactly the correct boundary conditions anyway. In condensed matter physics plane waves contrast with using LCAO as basis functions.

10.5 Pseudopotentials

A drawback to using plane waves is that electron wavefunctions don’t actually look much like plane waves, so the basis set is very different from the wavefunctions, and very many Fourier

components are required. One way around this is to use a ‘pseudopotential’ which attempts to describe the potential due to the nucleus and tightly bound shells of ‘core’ electrons which do not take part in bonding. In silicon for example the pseudopotential describes the nucleus and the $1s2s2p$ electrons.

The pseudopotential can be deduced from properties of the perfect atom: Consider:

$$V(r)\Phi(\mathbf{r}) = E + \frac{\hbar^2 \nabla^2}{2m} \Phi(\mathbf{r})$$

Where we know atomic properties E and $\Phi(r)$, but not $V(r)$, the potential seen by the outer electrons. We can invert the Schroedinger problem, solving for $V(r)$ to give the exact $\Phi(r)$ outside some core radius $r > r_c$, but smoothing it out for $r < r_c$.

In most applications involving chemical binding, the wavefunction only changes in the region outside r_c . So although the pseudowavefunction is not the correct Kohn-Sham eigenfunction, changes in its energy due to interaction with other electrons and ions are the same as the change in the Kohn-Sham eigenfunction.

Choosing r_c and inverting the Schroedinger equation is non-unique, but in general:

Pseudopotentials depend on the l quantum number, because they must include the fact that, e.g. $3s$ must be radially orthogonal to $1s$ and $2s$, while $3d$ are automatically so because of the angular dependence. This is called non-locality.

The core charge produced by the pseudo wavefunctions must be the same as that produced by the atomic wavefunctions. This ensures that the pseudo atom produces the same scattering properties as the ionic core.

Pseudo-electron eigenvalues must be the same as the valence eigenvalues obtained from the atomic wavefunctions.

Pseudo wavefunctions must be continuous at the core radius as well as its first and second derivative and also be non-oscillatory.

If you find it surprising that this works - it is! However tens of thousands of calculations give energies correct to within a few percent, so the approach seems to accord well with reality.

10.6 k-point sampling

DFT reduces the problem of 10^{26} interacting electrons to 10^{26} noninteracting quasiparticles. To reduce this to a manageable number, we recall that electrons in solids can be labelled by a wavevector \mathbf{k} , and that they form bands in which electrons with similar \mathbf{k} have similar energy. The energy is the integral of these, thus we can obtain a good estimate by sampling states from an evenly-spaced grid of “ \mathbf{k} -points”. As this grid becomes finer, so the accuracy of the integral improves. For most systems a surprisingly small number suffices: tens for insulators and hundreds for metals.

According to the Bloch theorem, any wavefunction must be written:

$$\Phi_{\mathbf{k}} = u(\mathbf{r}) \exp -i\mathbf{k} \cdot \mathbf{r}$$

If the wavefunction is expanded in plane waves, then

$$\Phi_{\mathbf{k}} = \sum_{\mathbf{b}} \exp -i(\mathbf{k} + \mathbf{b}) \cdot \mathbf{r}$$

where k correspond to Bloch waves longer than the unit cell, and b to basis function plane waves shorter than the cell (i.e. $b > k$).

10.7 A continuum of quantum states: quantum numbers in a crystal

In a crystal quantum states can be indexed by the Bloch quantum number k . In the LCAO approximation, there is a state for each possible atomic orbital at each value of \mathbf{k} . As the number of electrons tends to infinity, the allowed \mathbf{k} 's form a continuum. The most important application of quantum mechanics in solid state physics is to understand the relationship between energy and momentum. A graph of energy vs momentum is called a band structure.

States are occupied from the lowest energy upwards according to the exclusion principle. The set of momenta which correspond to the maximum allowed energy form a surface in the 3-d space - the so-called Fermi Surface.

Shown is the valence “band structure” of dhcp potassium calculated using DFT and pseudopotentials: letters are crystallographic notation for values of \mathbf{k} ($\Gamma = (0, 0, 0)$, others are on the edge of the Brillouin zone). Note the free electron parabola around Γ , as $E = \hbar^2 k^2 / 2m$. This structure has four layers of atoms per unit cell, so *on average* there are two bands below the Fermi surface at each k -point (each is spin degenerate). There are lots of bands crossing the Fermi level, showing that electrons can move from one state to another without requiring energy: potassium is a metal. Γ -A is quite a short distance in k -space, corresponding to waves along the long direction in the unit cell: the band structure appears like a parabola “folded back” on itself.

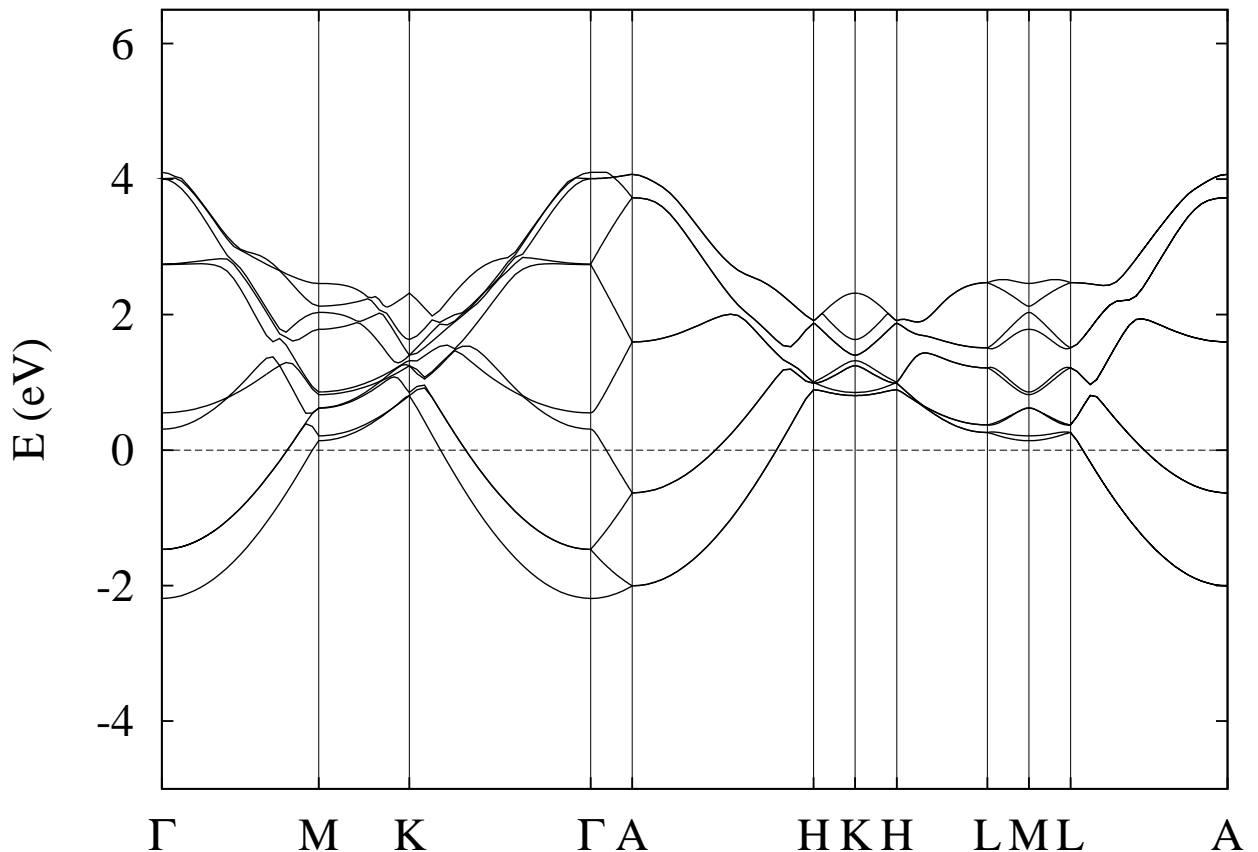


Figure 6: Band structure of potassium, energy scaled so that $E_F=0$. x-axis labels denote a path through the 3d space of \mathbf{k} -vectors.

11 Fundamentals of Quantum Scattering Theory

11.1 Centre of Mass Frame and the Two-body Problem

The problem of a particle in a given potential can be solved classically from Newton's equations. The Schroedinger equation can be used to describe the behaviour of one particle in a field.

The problem of two particles interacting via conservative fields can be reformulated into two parts: the behaviour of the centre of mass and the behaviour of the relative velocities of the particles. If we work in the centre of mass frame (COM), then the behaviour of the centre of mass is trivial, and we need worry only about the relative motions. This can be described by a *single* effective particle with effective mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$. This effective particle can then be treated with one particle equations.

The problem of three interacting particles cannot be reduced in this way. Hence the 'three-body-problem' is in general insoluble.

The COM transformation allows us to treat the scattering problem as a one body problem. For scattering problems we work in the COM frame, describing two real particles as an effective particle moving in a potential. Do not forget that for any experiment we will have to apply the above transformation to relate theory to the experimental results, though if the target particle is much heavier than the other the transformation may be slight. Note also that this transformation is invalid if there is an external field.

11.2 Some terminology for general scattering

The incident flux (I) of particles with momentum $\mathbf{p} = \hbar \mathbf{k}$ is the number of incident particles crossing unit area perpendicular to the beam direction per unit time.

The scattered flux (S) of particles with momentum $\mathbf{p}' = \hbar \mathbf{k}'$, is the number of scattered particles scattered into the element of solid angle $d\Omega$ about the direction θ, ϕ per unit time per unit solid angle.

The differential cross section is the ratio of the scattered flux in direction θ, ϕ to the incident flux.

$$\frac{d\sigma}{d\Omega} = S/I$$

The total cross section is the ratio of the scattered flux in any direction to the incident flux.

$$\sigma_T = \int \int \frac{d\sigma}{d\Omega} \sin \theta d\theta d\phi$$

11.3 Scattering in one dimension- Step function

Firstly, we review the problem of scattering by a step function in one dimension. Consider a particle moving from a region ($x < 0$) where the potential is $V = 0$ to a region ($x > 0$) where the potential is $V = V_0$.

Assuming the particle energy $E > V_0$, this is simply the free particle problem, the spatial solution to which is:

$$\Phi = A \exp(ikx) + B \exp(-ikx) \quad (x < 0); \quad \Phi = C \exp(ik'x) + D \exp(-ik'x) \quad (x > 0)$$

where $k = \sqrt{2mE}/\hbar$ and $k' = \sqrt{2m(E - V_0)}/\hbar$

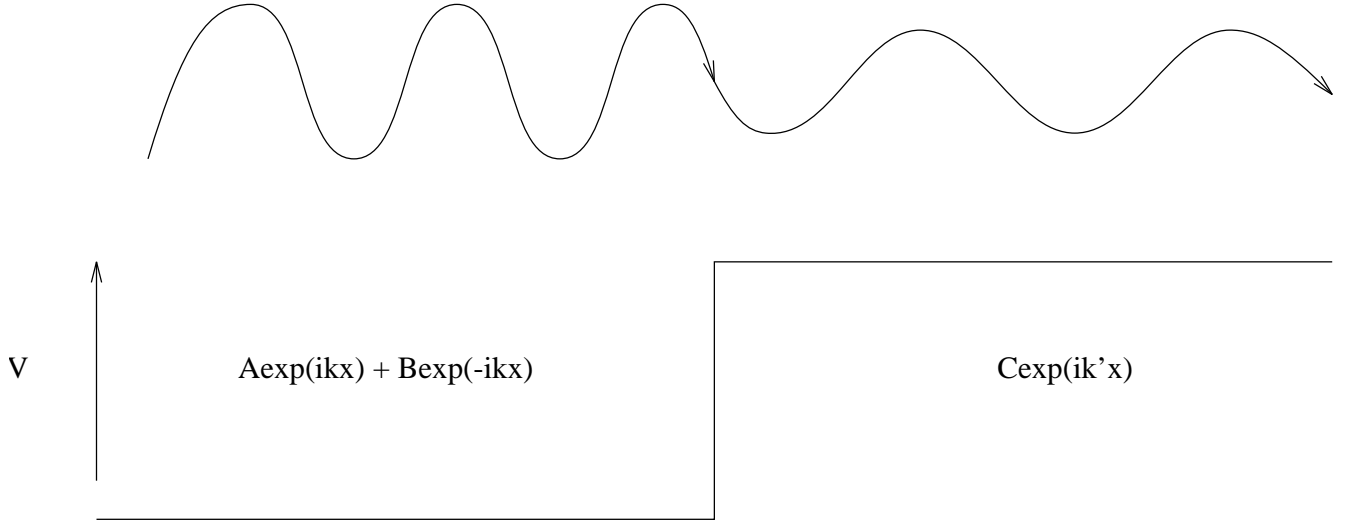


Figure 7: Scattering at a step function.

From the boundary condition that all particles start from $x = -\infty$, we can immediately set $D=0$. From the condition of continuity of Φ and $d\Phi/dx$ at $x = 0$ we also require $A + B = C$ and $k(A - B) = k'C$

This gives the reflected amplitude $B/A = (k - k')/(k + k')$ and the transmitted amplitude $C/A = 2k/(k + k')$

The reflected flux is thus

$$\frac{\hbar k}{m} A^2 \left(\frac{k - k'}{k + k'} \right)^2$$

and the transmitted flux is

$$\frac{\hbar k'}{m} A^2 \left(\frac{2k}{k + k'} \right)^2$$

Note that $A^2 \neq B^2 + C^2$. The conserved quantity is the *flux* of particles, not the probability density. In this case the transmitted particles are moving more slowly than the incident ones.

Notice that if V_0 is negative, the transmitted flux gets smaller as $|V_0|$ gets larger: it is difficult to fall off a big cliff! This anomaly is due to the unphysical potential - the discontinuous first derivative at $x = 0$.

We have not considered the case of $E < V_0$. Now the square root is imaginary and $\Phi(x > 0) = Ce^{-\kappa'x}$ where we define a *real* quantity $\kappa' = ik' = \sqrt{2m(V_0 - E)}/\hbar$. The boundary conditions are then $A + B = C$ and $ik(A - B) = \kappa'C$, which gives the reflected amplitude $B/A = (ik - \kappa')/(ik + \kappa')$ and the transmitted amplitude $C\kappa'/Ak = 2ik/(ik + \kappa')$.

Now the reflected flux is equal to the incident flux, and although the wavefunction penetrates the region $x > 0$, it decays exponentially and there is no propagating wave.

11.4 Scattering in one dimension - Square Well

The square well potential has $V(x < 0) = V(x > a) = 0$; $V(0 < x < a) = V_0$. As with the step function, we can write the wavefunction as a plane wave in each of the three regions.

$$\begin{aligned}\Phi(x < 0) &= A \exp(ikx) + B \exp(-ikx) \\ \Phi(0 < x < a) &= F \exp(ik'x) + G \exp(-ik'x) \\ \Phi(x > a) &= C \exp(ikx) + D \exp(-ikx)\end{aligned}$$

Once again there is no wave coming back from $x = \infty$ ($D = 0$).

There are now four boundary conditions from continuity of the wave function and its derivative at $x=0$ and $x=a$. The solving of four equations in four unknowns is straightforward but tedious. Eventually one can obtain ratios for reflected and transmitted flux:

$$\begin{aligned}B/A &= \frac{(k^2 - k'^2)(1 - e^{2ik'a})}{(k + k')^2 - (k - k')^2 e^{2ik'a}} \\ C/A &= \frac{4kk' e^{i(k'-k)a}}{(k + k')^2 - (k - k')^2 e^{2ik'a}}\end{aligned}$$

where $k^2 = 2mE/\hbar^2$ and $k'^2 = 2m(E - V_0)/\hbar^2$. Since the wavenumber is the same on both sides of the barrier, the reflection and transmission coefficients are just:

$$\begin{aligned}|B/A|^2 &= \left[1 + \frac{4k^2 k'^2}{(k^2 - k'^2)^2 \sin^2 k'a} \right]^{-1} = \left[1 + \frac{4E(E - V_0)}{V_0^2 \sin^2 k'a} \right]^{-1} \\ |C/A|^2 &= \left[1 + \frac{(k^2 - k'^2)^2 \sin^2 k'a}{4k^2 k'^2} \right]^{-1} = \left[1 + \frac{V_0^2 \sin^2 k'a}{4E(E - V_0)} \right]^{-1}\end{aligned}$$

We get complete transmission when $k'a = n\pi$, i.e. when an exact number of half waves fit in the well.

Assuming that $E > V_0$. Looking at the limits of this, we see that as $E \rightarrow V_0$ then $\sin^2(k'a) \rightarrow k'a$ and the transmission coefficient

$$|C/A|^2 \rightarrow \left[1 + \frac{mV_0 a^2}{2\hbar^2} \right]^{-1}$$

As the incoming particle energy is increased, the transmission oscillates between $\left[1 + \frac{V_0^2}{4E(E - V_0)} \right]^{-1}$ and 1 at $k'a = n\pi$. The lower limit itself increases to 1 as E increases.

For the tunnelling case where $E < V_0$ we can use these solutions for B/A and C/A , except that k' is now imaginary. This gives

$$|C/A|^2 = \left[1 + \frac{4E(E - V_0)}{V_0^2 \sinh^2 |k'|a} \right]^{-1}$$

which decreases monotonically with decreasing E . Thus a small change in V_0 can give a large change in $|C/A|^2$. This is the principle on which the transistor and the tunnelling electron microscope are based.

Note that the transmitted wave $\Phi(x > a) = C \exp(ikx)$, differs from the incident wave only by a phase - it has the same wavevector. Thus the only effect of the potential on the transmitted particles is to change their *phase*, an idea we shall meet again.

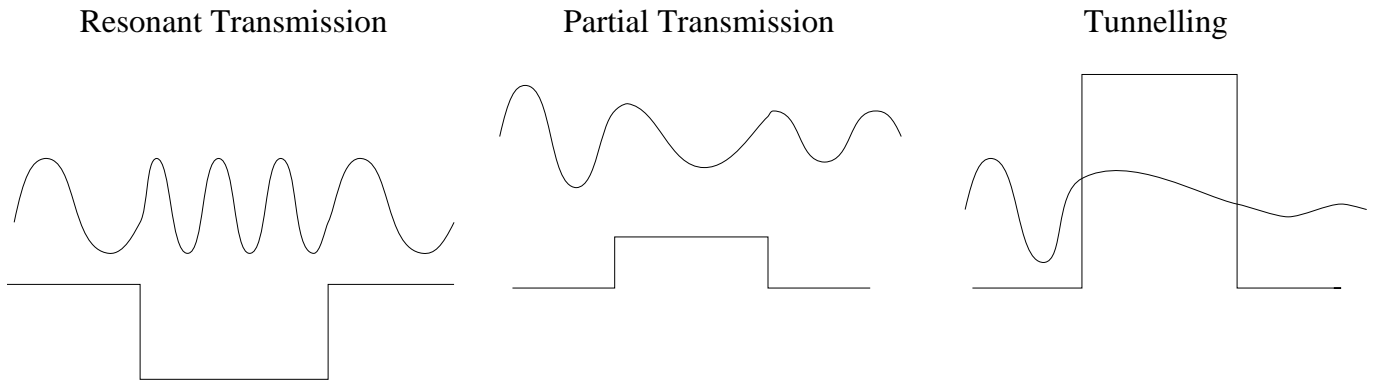


Figure 8: Forward moving wavefunctions passing a square well potential

11.5 The transistor (1956 Nobel) and giant magneto-resistance (2007 Nobel)

Transistors can be modelled as a barrier potential, with the voltage across them represented by different potentials on either side.

The rapid variation in transmission coefficient (current) with change in potential barrier (voltage) is the basis of the transistor. The name comes from 'transfer resistor'. The resistance to motion of electrons past the barrier is determined by the voltage V_0 in the barrier region more than the voltage difference across the transistor.

Actual behaviour also depends on the availability of electrons for conduction, which depends in turn on the material in question, since there must be available electron states of appropriate energy on each side of the barrier.

In GMR a series of barriers are created from layers of ferromagnetic material and a spacer chosen to make the layer align antiferromagnetically (e.g. FeCrFe). Conduction electrons with spin opposite to the magnetic moment pass easily through iron (there are many states available to them). So oppositely aligned layers form a series of barriers to either spin. An external magnetic field applied to the GMR causes all the ferromagnetic layers to align, meaning there is no barrier to antialigned conduction electrons. Thus a magnetic field causes a change in resistance: GMR heads are used to "read" the magnetisation states in computer hard disks.

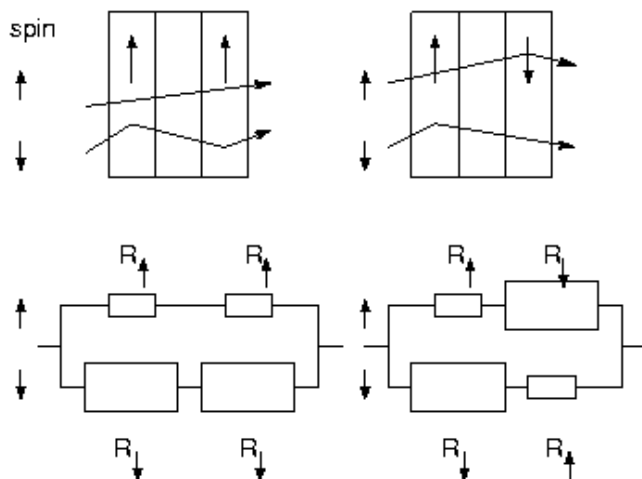


Figure 9: Giantmagnetoresistance

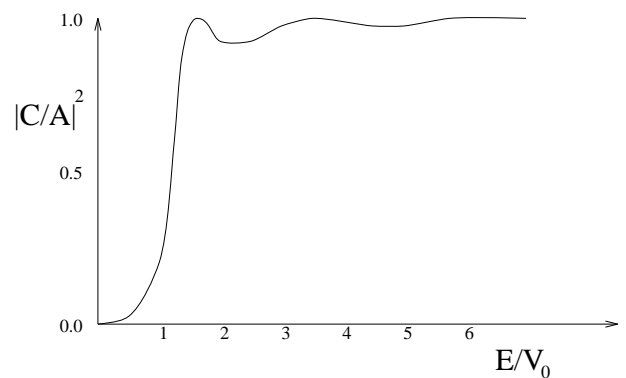


Figure 10: Transmission in a 1D square well

12 Scattering in three dimensions

12.1 Cross sections and geometry

Most experiments in physics consist of sending one particle to collide with another, and looking at what comes out.

The quantity we can usually measure is the scattering cross section: by analogy with classical scattering of hard spheres, we assuming that scattering occurs if the particles ‘hit’ each other. The cross section is the apparent ‘target area’. The total scattering cross section can be determined by the reduction in intensity of a beam of particles passing through a region on ‘targets’, while the differential scattering cross section requires detecting the scattered particles at different angles.

We will use spherical polar coordinates, with the scattering potential located at the origin and the plane wave incident flux parallel to the z direction. In this coordinate system, scattering processes are symmetric about ϕ , so $\frac{d\sigma}{d\Omega}$ will be independent of ϕ .

We will also use a purely classical concept, the impact parameter b which is defined as the distance of the incident particle from the z -axis prior to scattering.

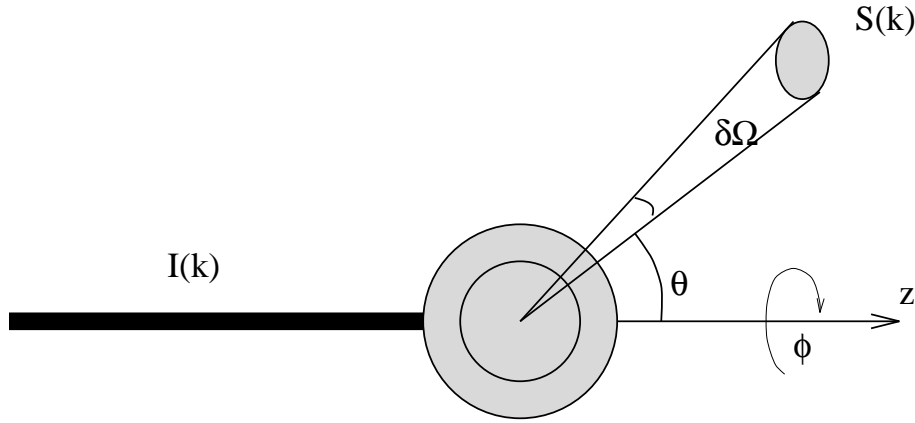


Figure 11: Standard spherical coordinate geometry for scattering

12.2 The Born Approximation

We can use time-dependent perturbation theory to do an approximate calculation of the cross-section. Provided that the interaction between particle and scattering centre is *localised* to the region around $r = 0$, we can regard the incident and scattered particles as free when they are far from the scattering centre. We just need the result that we obtained for a *constant* perturbation, Fermi’s Golden Rule, to compute the rate of transitions between the initial state (free particle of momentum \mathbf{p}) to the final state (free particle of momentum \mathbf{p}').

The Hamiltonian for a single particle being scattered by a fixed potential as

$$\hat{H} = \hat{H}_0 + \hat{V}(\mathbf{r}) \quad \text{where} \quad \hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m}, \text{ the kinetic energy operator}$$

and treat the potential energy operator, $\hat{V}(\mathbf{r})$, as the perturbation inducing transitions between the eigenstates of \hat{H}_0 , which are plane waves.

If we label the initial and final plane-wave states $\Phi_{in} = \exp(i\mathbf{k} \cdot \mathbf{r} - i\omega t)$ and $\Phi_{scat} = \exp(i\mathbf{k}' \cdot \mathbf{r} - i\omega' t)$ by their respective wave-vectors, then Fermi’s Golden Rule for the rate of transitions is

$$R = \frac{2\pi}{\hbar} |\langle \mathbf{k}' | \hat{V} | \mathbf{k} \rangle|^2 g(E_k)$$

where $g(E_k)$ is the density of final states; $g(E_k)dE_k$ is the number of final states with energy in the range $E_k \rightarrow E_k + dE_k$.

The quantity $\langle \mathbf{k}' | \hat{V} | \mathbf{k} \rangle$ is known as the *matrix element* of the perturbation and is usually abbreviated thus

$$V_{\mathbf{k}'\mathbf{k}} \equiv \langle \mathbf{k}' | \hat{V} | \mathbf{k} \rangle = \int \int \int u_{\mathbf{k}'}^*(\mathbf{r}) V(\mathbf{r}) u_{\mathbf{k}}(\mathbf{r}) d\tau.$$

The time variation has been suppressed here. For constant potential, the only non-zero terms come from $\omega = \omega'$: elastic scattering. For a time oscillating potential (e.g. $V(\mathbf{r}) \sin \omega_0 t$) the non-zero contribution comes from $\omega = \omega' \pm \omega_0$: inelastic scattering where the scattered particle gains/loses a quantum of energy from/to the system providing the potential.

12.3 Box Normalisation and Density of Final States

Plane-wave states have wavefunctions of the form: $u_{\mathbf{k},\omega}(\mathbf{r}) = C \exp(i(\mathbf{k} \cdot \mathbf{r} - \omega t))$ with C a normalisation constant. Because plane-wave states are not properly normalisable we employ the trick of normalising them in a large (relative to potential range) cubic box of side L with periodic boundary conditions. We then take the limit $L \rightarrow \infty$ at the end of the calculation.

Thus we require that

$$\int \int \int_{\text{box}} u_{\mathbf{k},\omega}^*(\mathbf{r}) u_{\mathbf{k},\omega}(\mathbf{r}) d\tau = |C|^2 \int \int \int_{\text{box}} d\tau = |C|^2 L^3 = 1$$

giving for the normalised eigenfunctions: $u_{\mathbf{k},\omega}(\mathbf{r}) = L^{-3/2} \exp(i\mathbf{k} \cdot \mathbf{r} - \omega t)$

Of course, enclosing the system in a finite box has the consequence that the allowed momentum eigenvalues are no longer continuous but *discrete*. With periodic boundary conditions

$$u(-\frac{L}{2}, y, z) = u(\frac{L}{2}, y, z), \quad \text{etc.}$$

the momentum eigenvalues are forced to be of the form

$$\mathbf{p} \equiv \hbar \mathbf{k} = \frac{2\pi\hbar}{L} (n_x, n_y, n_z), \quad \text{with } n_x, n_y, n_z = 0, \pm 1, \pm 2, \dots$$

For sufficiently large L , we can approximate the continuous spectrum arbitrarily closely.

Any possible final-state wave-vector, \mathbf{k} , corresponds to a point in *wave-vector* space with coordinates (k_x, k_y, k_z) . The points form a cubic lattice with lattice spacing $2\pi/L$. Thus the volume of k -space per lattice point is $(2\pi/L)^3$, and the number of states in a volume element $d^3\mathbf{k}$ is

$$\left(\frac{L}{2\pi}\right)^3 d^3\mathbf{k}' = \left(\frac{L}{2\pi}\right)^3 k^2 dk d\Omega$$

We require $g(E_k)$, the density of states per unit energy, where: $E_k = \hbar^2 k^2 / 2m$ is the energy corresponding to wave-vector \mathbf{k}' . Now, the wave-vectors in the range $\mathbf{k}' \rightarrow \mathbf{k}' + d^3\mathbf{k}'$ correspond to the energy range $E_k \rightarrow E_k + dE_k$, so that

$$g(E_k) dE_k = \left(\frac{L}{2\pi}\right)^3 k^2 dk d\Omega$$

is the number of states with energy in the desired interval and with wave-vector, \mathbf{k}' , pointing into the solid angle $d\Omega$ about the direction (θ, ϕ) . Noting that $dE_k = (\hbar^2 k / m) dk$ yields the final result for the density of states,

$$g(E_k) = \frac{L^3 m k}{8\pi^3 \hbar^2} d\Omega$$

12.4 Incident and Scattered Flux

The box normalisation corresponds to one particle per volume L^3 , so that the number of particles crossing unit area perpendicular to the beam per unit time is just given by the magnitude of the incident velocity divided by L^3 :

$$\text{incident flux} = \frac{|\mathbf{p}|/m}{L^3} = \frac{\hbar k}{mL^3}$$

Using the Golden Rule, we have that the rate of transitions between the initial state of wave-vector \mathbf{k} and final states whose wave-vectors \mathbf{k}' lie in the element of solid angle $d\Omega$ about the direction (θ, ϕ) of the wave-vector \mathbf{k}' , is given by

$$R = \frac{2\pi}{\hbar} |V_{\mathbf{k}'\mathbf{k}}|^2 \frac{L^3}{8\pi^3} \frac{mk}{\hbar^2} d\Omega$$

but this is just the number of particles scattered into $d\Omega$ per unit time. To get the scattered flux we simply divide by $d\Omega$ to get the number per unit time per unit solid angle.

12.5 The Differential Cross-Section

We now have all the ingredients, the scattered flux and the incident flux, to compute the cross-section:

$$\frac{d\sigma}{d\Omega} \equiv \frac{\text{scattered flux}}{\text{incident flux}} = \frac{mL^3}{\hbar k'} \frac{2\pi}{\hbar} |V_{\mathbf{k}'\mathbf{k}}|^2 \frac{L^3}{8\pi^3} \frac{mk}{\hbar^2}$$

Noting that, for *elastic scattering*, $k' = k$, we obtain finally the so-called Born approximation for the differential cross-section:

$$\frac{d\sigma}{d\Omega} = \frac{m^2}{4\pi^2\hbar^4} L^6 \left| \langle \mathbf{k}' | \hat{V} | \mathbf{k} \rangle \right|^2$$

where the matrix element $V_{\mathbf{k}'\mathbf{k}} \equiv \langle \mathbf{k}' | \hat{V} | \mathbf{k} \rangle$ is given by

$$\langle \mathbf{k}' | \hat{V} | \mathbf{k} \rangle = \frac{1}{L^3} \int \int \int V(\mathbf{r}) \exp(-i\chi \cdot \mathbf{r}) d\mathbf{r}$$

with $\chi \equiv \mathbf{k}' - \mathbf{k}$, the so-called *wave-vector transfer*. Thus the required matrix element in the Born approximation is just the 3-dimensional Fourier transform of the potential energy function. The total scattering cross section is simply:

$$\sigma_T = \int \frac{d\sigma}{d\Omega} d\Omega = \int \int \frac{d\sigma}{d\Omega} \sin\theta d\theta d\phi$$

Observe that the final result for the differential cross-section is independent of the box size, L , which we used to normalise the plane-wave states.

12.6 Further Simplification to 1D for Conservative, Central Potential

Consider a central potential $V(\mathbf{r}) = V(|\mathbf{r}|)$ where energy is conserved $|\mathbf{k}'|^2 = |\mathbf{k}|^2$. Here χ is a vector of length $2k \sin \frac{\theta}{2}$ where θ is the scattering angle.

We can make some progress with the matrix element integral if we choose a polar coordinate system with χ along the z -axis, so that $\chi \cdot \mathbf{r} = \chi r \cos\theta$. Since we are trying to integrate over all space this change does not affect the limits of the integral.

$$\begin{aligned} V_{\mathbf{k}'\mathbf{k}} &= \int_0^{2\pi} d\phi \int_{-1}^{+1} \int_0^\infty V(r) e^{-i\chi r \cos\theta} r^2 dr d(\cos\theta) \\ &= 2\pi \int_0^\infty \frac{e^{-i\chi r} - e^{i\chi r}}{-i\chi r} V(r) r^2 dr = \frac{4\pi}{\chi} \int_0^\infty r V(r) \sin(\chi r) dr \end{aligned}$$

But since $|\mathbf{k}| = |\mathbf{k}'|$, $|\chi| = 2k \sin \frac{\theta}{2}$, Whence we obtain the most useful form of the Born approximation:

$$\frac{d\sigma}{d\Omega} = \frac{m^2}{(k \sin \frac{\theta}{2})^2 \hbar^4} \left| \int_0^\infty r V(r) \sin(2kr \sin \frac{\theta}{2}) dr \right|^2$$

Thus the scattering cross-section is independent of ϕ (due to cylindrical symmetry of the problem). Note that this shows that the differential cross section does not depend on scattering angle and beam energy independently, but on a single parameter χ . By using a range of energies for the incoming particles, k , this dependence can be used to test whether experimental data can be well described by the Born Approximation.

The most common use of the Born approximation is, of course, in reverse. Having found $\frac{d\sigma}{d\Omega}$ experimentally, a reverse Fourier transform can be used to obtain the form of the potential.

12.7 Example of Born Approximation

Consider scattering of particles interacting via a 3D square well potential: $V(r < a) = V_0$; $V(r > a) = 0$.

The integral required here is then (with $\chi = 2k \sin \frac{\theta}{2}$):

$$\int_0^a r V_0 \sin(\chi r) dr = \left[\frac{\sin(\chi r) - \chi r \cos(\chi r)}{\chi^2} \right]_0^a$$

whence:

$$\frac{d\sigma}{d\Omega} = \left[\frac{2\mu V_0}{\chi \hbar^2} \right]^2 \left[\frac{\sin(\chi a) - \chi a \cos(\chi a)}{\chi^2} \right]^2$$

Using a Maclaurin expansion, the low energy limit is:

$$\frac{d\sigma}{d\Omega} = \left[\frac{2\mu V_0}{\chi \hbar^2} \right]^2 \frac{1}{9} \left[1 - \frac{1}{5} \chi^2 a^2 \right]$$

From integrating over θ and ϕ the low and high energy limits for the total cross section are

$$\sigma(E \rightarrow \infty) = 2\pi \left[\frac{\mu}{\hbar^2} \right]^2 \left[\frac{V_0 a^3}{ka} \right]^2 \quad \sigma(E \rightarrow 0) = 2\pi \left[\frac{\mu}{\hbar^2} \right]^2 \left[\frac{V_0 a^3}{ka} \right]^2 \frac{8}{9} (k^2 a^2 - \frac{2}{5} k^4 a^4 + \dots)$$

12.8 General Notes on Scattering in the Born Approximation

The square well illustrates some general feature of scattering in the Born approximation:

- Born approximation is based on perturbation theory, so works best for high energy particles.
- Scattering depends on V_0^2 , so both attractive and repulsive potentials behave the same.
- At high energy, cross section is inversely proportional to the energy ($E = \hbar^2 k^2 / 2m$)
- Dependence on k and θ arises only through the combination $\chi = 2k \sin \frac{\theta}{2}$. Thus as energy increases, the scattering angle θ is reduced and the scattered beam becomes more peaked in the 'straight on' direction.
- Angular dependence depends on the range of the potential a but not on the strength V_0 .
- Total cross section depends on both range a and depth V_0 of the potential.

13 Further Concepts in Quantum Scattering Theory

13.1 Born Series, Green Functions - A Hint of Quantisation of the Field

Solving the Schroedinger equation using Green Functions automatically gives a solution in a form appropriate for scattering. By making the substitution $E = \hbar^2 k^2 / 2\mu$ and $U(r) = (2\mu/\hbar^2)V(r)$ we can write the TISE as:

$$[\nabla^2 + k^2]\Phi = U(r)\Phi$$

For $U(r) = 0$ this gives $\phi_0(r) = Ae^{i\mathbf{k}\cdot\mathbf{r}}$, a travelling wave. We now introduce a ‘Green’s Function’ for the operator $[\nabla^2 + k^2]$, which is the solution to the equation:

$$[\nabla^2 + k^2]G(r) = \delta(r)G(r) \quad G(r) = -\exp(ikr)/4\pi r$$

$\delta(r)$ is the Dirac delta-function as is $\delta(r)G(r)$, since $G(r)$ diverges at the origin. $G(r)$ has the property that any function Φ which satisfies

$$\Phi(r) = \phi_0(r) + \int G(r-r')U(r')\Phi(r')d^3r'$$

where $\phi_0(r)$ is the free particle solution, will be a solution to the TISE. Since $\phi_0(r)$ is the unscattered incoming wave, the second term must represent the scattered wave.

Thus the general solution to the TISE is given by:

$$\Phi(r) = Ae^{i\mathbf{k}\cdot\mathbf{r}} + \int G(r-r')U(r')\Phi(r')d^3r'$$

In this expression, Φ appears on both sides. We can substitute for Φ using the same equation:

$$\Phi(r) = Ae^{i\mathbf{k}\cdot\mathbf{r}} + \int G(r-r')U(r')Ae^{i\mathbf{k}\cdot\mathbf{r}'}d^3r' + \int \int G(r-r')U(r')G(r'-r'')U(r'')\Phi(r'')d^3r'd^3r''$$

Repeated substitutions gives the *Born series*, terminated by a term involving $\Phi(r)$ itself. If the potential is weak, the higher order terms can be ignored. The first order term is just the matrix element between the incoming plane wave and the Green function: the Born approximation again! If we think of the potential U as an operator, the first term represents the incoming wavefunction

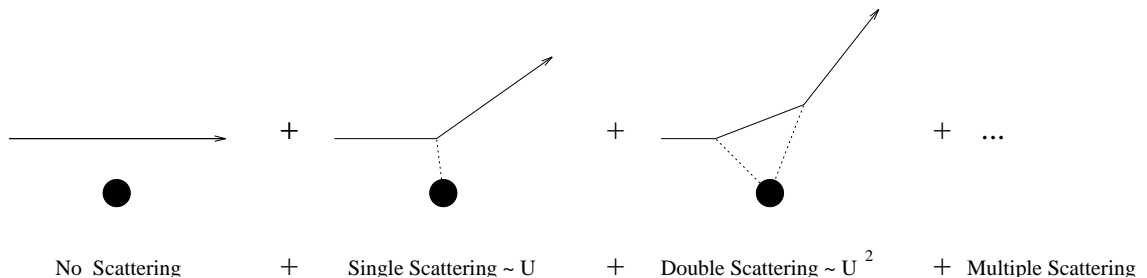


Figure 12: Born Series - scattering as series of terms

being operated on once. The second term represents the incoming wavefunction being operated on twice. And so forth. This suggests a way of *quantising* the effect of the field: The first order term corresponds to a single scattering event, the second order term to double scattering etc.

13.2 Scattering of distinguishable particles and identical particles

Consider two beams of distinguishable particles with the same mass colliding, and scattering through some angle θ . Let the intensity of the scattered particles have angular dependence $|f(\theta)|^2$. Conservation of energy and momentum ensure that the scattering angles are the same for both particles in the COM frame. As usual, the radial part of the wavefunction far from the region of interaction is simply a plane wave so the wavefunction can be written as a function of θ .

The intensity for the process in which both particles are scattered through an angle $(\pi - \theta)$ is $|f(\pi - \theta)|^2$. Note that this process results in particles arriving in the same places as with $f(\theta)$ - it is just the other particles (see diagram).

If the two particle beams are distinguishable they cannot interfere and differential cross section for either particle to be detected at θ is:

$$I_{dis} = |f(\theta)|^2 + |f(\pi - \theta)|^2$$

If, however, the particles are indistinguishable bosons(fermions), they can interfere and the combined wavefunction must (anti)symmetric under exchange of labels:

$$\Phi_{fer}^{bos} = f(\theta) \pm f(\pi - \theta) \qquad I_{fer}^{bos} = |f(\theta) \pm f(\pi - \theta)|^2$$

Taking the specific extreme example of scattering through $\pi/2$, the differential cross section is $2|f(\pi/2)|^2$ for distinguishable particles, $4|f(\pi/2)|^2$ for identical bosons, and 0 for identical fermions.

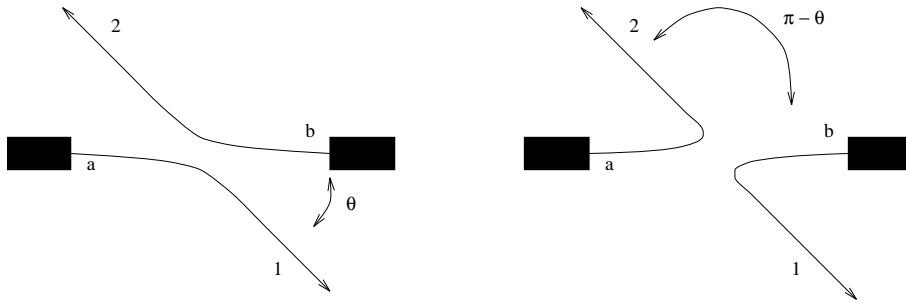


Figure 13: Two indistinguishable scattering processes.

13.3 Scattering of indistinguishable particles into the same state

Consider scattering of two indistinguishable bosons by an external potential. The wavefunction describing the bosons must be *symmetric* with respect to exchange. Thus the cross section for scattering of both through the same angle is: $|2f(\theta)|^2$: two bosons are twice as likely to be scattered into the same state as two distinguishable particles. For many bosons the effect is even more pronounced, and the probability of scattering *out* of the state is similarly reduced.

The tendency for bosons to clump into one state leads to superfluid behaviour in He^4 and superconductivity: α particles and Cooper pairs behave as bosons. All the particles are in the same state and cannot be scattered out.

For fermions, the cross section for being scattered into the same state is $|f(\theta) - f(\theta)|^2 = 0$, as we would expect from the exclusion principle.

13.4 Collision between two unpolarised electron beams

In this case, half the collisions will be between like-polarised electrons, so will involve interference, and half will be between unlike electrons: so there would be no interference. In both cases $|f(\theta)|^2$ represents Rutherford scattering. The differential cross section of finding an electron scattered through an angle θ is thus:

$$I = \frac{1}{2}(I_{dis} + I_{ind}) = \frac{1}{2}(|f(\theta)|^2 + |f(\pi - \theta)|^2) + \frac{1}{2}|f(\theta) - f(\pi - \theta)|^2$$

Consider $\theta = \pi/2$. The like polarised beams give zero probability, so unpolarised beams give only half what we would expect from Coulomb scattering of distinguishable particles. Furthermore, the spins of pairs of electrons scattered through $\theta = \pi/2$ are always observed to be opposite.

An alternate philosophy is that we should treat the spins as a symmetric triplet and an antisymmetric singlet, with probabilities $\frac{3}{4}$ and $\frac{1}{4}$. Then the spatial scattering process must be antisymmetric in the first case and symmetric in the second. This gives the same answer!

13.5 Scattering of identical free particles with a periodic potential

For a free particle moving in a 1D region of space there are two degenerate wavefunctions ($\Phi = e^{\pm ikx}$). If there is a weak periodic potential, $V \cos ax$, to evaluate the energy shift to first order in degenerate perturbation theory the relevant matrix elements are:

$$\int e^{\pm ikx} V \cos ax e^{\mp ikx} dx = \int V \cos ax dx = 0; \quad \int e^{\pm ikx} V \cos ax e^{\pm ikx} dx = \int V \cos ax \cos 2kx dx$$

The second term is also zero, except in the case $2k = a$. This gives rise to the remarkable result: *To first order, free particles are unaffected by a periodic potential unless it has half the wavelength.* This is the basis of Bragg's Law, x-ray and neutron diffraction.

13.6 Scattering of free electrons in metals

If we describe an electron bound in a solid or liquid as a free electron, we see that scattering occurs only for those electrons with wavenumbers close to periodic repeats. For simple metals (Li, Na etc) the highest occupied free-electron level has wavelength greater than any crystal spacing, so it only sees the average of the ionic potential.

To first order, only electrons with the periodicity of the lattice are scattered. To second order in perturbation theory, the potential can mix states:

$$\Delta E = \frac{|V_{ij}|^2}{(E_j - E_i)}; \quad V_{ij} = \int e^{\pm i(a/2+\delta)x} V \cos ax e^{\pm i(a/2-\delta)x} \neq 0$$

which gives significant energy shifts for states $\pm\delta$ from the lattice periodicity ($E_j - E_i = -\hbar^2 a\delta/m$). Thus free-electron levels with $k \approx a/2$ are split by periodic potentials giving a *bandgap* in the density of allowed states. At first glance, this may seem to be totally different physics from the LCAO band gaps we saw earlier. In fact, it's simply another manifestation of using two different *mathematical* basis sets to describe the same *physical* phenomenon.

13.7 Low energy Scattering: Partial Waves

The Born Approximation is a perturbation method based on the Fermi Golden Rule and is therefore valid when the incoming particle energy is large compared to the potential. An alternative approach is needed at low energy. For a central potential, scattering geometry plane wave in, radial wave out, implies a wavefunction:

$$|\Psi\rangle = \text{IncidentWave} + \text{ScatteredWave} = e^{ikz} + f(\theta)e^{ikr}/r$$

The incident flux is $I = ve^{iKz}e^{-iKz} = v = \hbar k/m$. The scattered flux must be a normalisable plane wave (hence e^{-iKr}/r), with a θ dependence arising from the scattering. By symmetry, there is no ϕ dependence. Thus the scattered flux per unit area will be: $vf^*(\theta)f(\theta)/r^2$. The cross section $d\sigma/d\Omega = S(\theta)/I = f^*(\theta)f(\theta)$, and all we need do is solve the Schroedinger equation and calculate $f(\theta)$.

For a spherically symmetric potential, the angular parts of the wavefunction are simply spherical harmonics, so scattering is described by the radial equation:

$$\frac{d^2 u_l(r)}{dr^2} - \frac{l(l+1)}{r^2} u_l(r) + \frac{2\mu}{\hbar^2} [E - V(r)] u_l(r) = 0$$

where $u_l(r) = rR_l(r)$, the same substitution as in the atomic hydrogen problem. Assuming a short range potential, $V(r \rightarrow \infty) = 0$, $R_l(Kr \rightarrow \infty)$ describes a free particle, with some phase $l\pi/2 - \delta_l$.

$$R_l(Kr) = \sin(Kr - l\pi/2 + \delta_l)/Kr$$

Thus the effect of the scattering at long range can be described by a set of *phase shifts* δ_l .

To solve further, we expand a plane wave into angular momentum components using a complete set of spherical harmonics and Bessel Functions:

$$\exp(iKr \cos \theta) = \sum_{l=0}^{\infty} i^l j_l(Kr) (2l+1) P_l(\cos \theta)$$

so that we can write:

$$\Psi(\mathbf{r}) = e^{iKz} + f(\theta) \frac{e^{iKr}}{r} = \sum_{l=0}^{\infty} i^l j_l(Kr) (2l+1) P_l(\cos \theta) + f(\theta) \frac{e^{iKr}}{r} = \sum_{l=0}^{\infty} b_l R_l(Kr) P_l(\cos \theta)$$

where b_l are expansion coefficients for the expression of Ψ in the *partial wave* basis, which can be determined from the boundary $r \rightarrow \infty$, giving:

$$f(\theta) = K^{-1} \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l} \sin \delta_l P_l(\cos \theta)$$

From this we can calculate $d\sigma/d\Omega = |f(\theta)|^2$ and $\sigma = 2\pi \int |f(\theta)|^2 d\theta$. Differential cross sections $d\sigma/d\Omega$ are complicated, involving many cross terms. However, when integrated over all θ these cross terms vanish due to orthogonality of the Legendre polynomials $\langle P_l | P_{l'} \rangle = 0$ ($l \neq l'$), and

$$\sigma = \frac{4\pi}{K^2} \sum_{l=0}^{\infty} (2l+1) \sin^2 \delta_l$$

Hence scattering cross sections are completely determined by $|K|$ and the phase shifts δ_l . This is most useful in the low energy limit (*S-wave scattering*) where any particle with $l > 0$ must be so far from the target (*impact parameter* $b = l/\hbar k$) that it will miss.

Note the term $(2l+1)$. This can be related to the classical ‘impact parameter’ mentioned above. The angular momentum of a particle of velocity v is $mbv = \sqrt{l(l+1)}\hbar$. Thus a classical (large l) particle with angular momentum $l\hbar$ would pass between a ring of radius $b = l\hbar/mv$ and one of radius $b = (l+1)\hbar/mv$. The area between these rings is $(2l+1)\pi(\hbar/mv)^2$ so for a uniform beam the probability of a particle having angular momentum l is proportional to $(2l+1)$.

14 Using Partial Waves

14.1 Impact Parameter and Classical Analogies

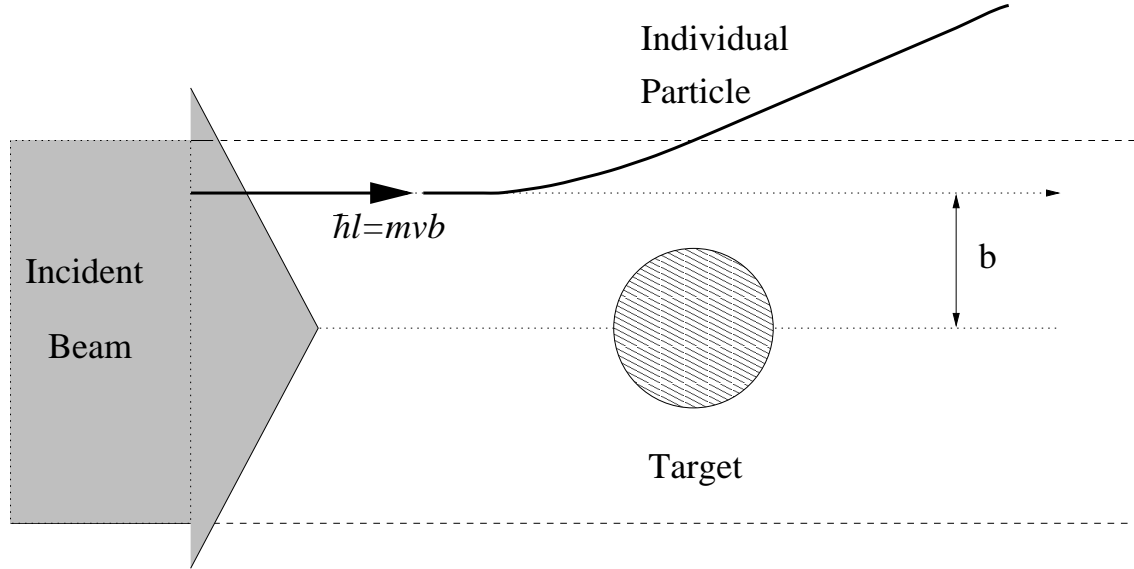


Figure 14: Relation between classical and quantum angular momentum

Knowing the impact parameter gives us some classical idea of whether a scattering event is likely. If the impact parameter is larger than the range of the potential, then classically the particles would miss. In the quantum case, we expect this to mean that the phase shift for that angular momentum is zero, and hence that the contribution from that term in the expansion is zero. Thus at a given incoming momentum, $\hbar k$, we can determine how many terms in the partial wave expansion to consider from $\hbar k b_{max} \approx l_{max} \hbar$, where b_{max} is the maximum impact parameter for classical collision, i.e. the range of the potential.

14.2 S-wave scattering

Although exact at all energies, the partial wave method is most useful for dealing with scattering of low energy particles. This is because for slow moving particles to have large angular momentum ($\hbar k b$) they must have large impact parameters b . Classically, particles with impact parameter larger than the range of the potential miss the potential. Thus for scattering of slow-moving particles we need only consider a few partial waves, all the others are unaffected by the potential ($\delta_l \approx 0$). Thus partial waves and the Born approximation are complementary methods, good for slow and fast particles respectively.

For very low energy we need consider only the first term in the partial wave expansion. This is known as *S-wave scattering*. In this case it is possible to solve for the differential cross section, since only the first term in the series for $f(\theta)$ is involved: Since the angular variation is $P_0(\cos \theta) = 1$ the scattering is isotropic.

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 = k^{-2} \sin^2 \delta_0$$

At higher energies, other angular momentum components come into play. For a given l component, scattering is maximised for $\delta_l = \pi/2$.

14.3 Resonance

In some cases where a potential has a bound state of particular angular momentum, the scattering of particle with that angular momentum will be especially enhanced. In such cases the total scattering cross section will show a peak, and the angular distribution will be characteristic of the appropriate $P_l(\cos \theta)$. This very strong scattering is known as resonance and is a powerful method for studying bound states.

14.4 Example of S-wave scattering - Attractive square well potential

An example where we can solve for the phase shift is the 3D-square well potential:

$$(V(r < R) = -V_0; V(r > R) = 0).$$

For the $l = 0$ case the radial equation with $U_0 = R_0 r$ is

$$\frac{d^2 u_0(r)}{dr^2} + \frac{2\mu}{\hbar^2} [E - V(r)] u_0(r) = 0$$

The solutions to this are familiar from the 1D square well. If we write

$$K_0 = \sqrt{2\mu[E + V_0]}/\hbar; \quad K = \sqrt{2\mu E}/\hbar$$

then for $r < R$, $u(r) = A \sin K_0 r + B \cos K_0 r$.

and for $r > R$, $u(r) = C \sin Kr + D \cos Kr$. which can easily be written in a different form to show the appropriate phase shift δ_0 : $u(r) = F \sin(Kr + \delta_0)$ where $(C = F \cos \delta_0 ; D = F \sin \delta_0)$

As with the 1D square well, the boundary conditions are that u and $\frac{du}{dr}$ are continuous at R , which lead to:

$$K \tan K_0 R = K_0 \tan(KR + \delta_0) \quad \text{or} \quad \delta_0 = \tan^{-1} \left(\frac{K}{K_0} \tan K_0 R \right) - KR$$

In the low energy case $KR \ll 1$, we obtain maximum scattering ($\sin^2 \delta_0 \rightarrow 1$) when $K_0 R = (n + \frac{1}{2})\pi$, when the scattering cross section is $\sigma = 4\pi/K^2$. This is an example of *s-wave resonance*.

In the same slow particle limit $K \ll K_0$, and assuming that $\tan K_0 R$ is not very large: $\delta_0 \approx \sin \delta_0$.

$$\sigma \approx 4\pi R^2 \left(\frac{\tan K_0 R}{K_0 R} - 1 \right)^2$$

This correctly predicts that when $\tan K_0 R = K_0 R$ the scattering cross section will be zero.

There are a few features of the square-well which also apply in more general cases. Assuming K_0 is basically a measure of the potential depth.

- For weak coupling $K_0 R \ll 1$, $\delta_0(K) \rightarrow 0$ as $K \rightarrow 0$
- When $K_0 R$ approaches $\pi/2$ the potential is almost able to bind an *s-wave* bound state. Now the phase shift $\delta_0(K) \rightarrow \pi/2$ and the cross section *diverges* like K^{-2} as $K \rightarrow 0$. This is known as zero energy resonance.
- If E is high enough that $\delta_l = (n + \frac{1}{2})\pi$ for $l \neq 0$ the scattering cross section can become especially high due to another angular momentum component - *p-wave* resonance for $l = 1$, *d-wave* resonance for $l = 2$ etc. In these cases the eigenfunction becomes large near to the potential. The potential is said to have *virtual states* at the resonance energies.

- *Levinson's Theorem* states that

$$\lim_{k \rightarrow 0} \delta_l(k) = n_l \pi$$

where n_l is the number of bound states with angular momentum l .

- Whenever $\delta_0(K) = n\pi$, for s -wave scattering, $\sigma = 0$. Thus for certain energies of the incoming particle, the scattering is extremely small. This condition can only be consistent with the condition for s -wave scattering ($KR \ll 1$) if the potential is attractive ($V_0 < 0$).
- $\delta_0(K)$ tends to decrease with increasing K . This can be understood physically as the faster particles having less time to interact and thus experiencing smaller phase shifts. As $K \rightarrow \infty$, $\delta_l(K) \rightarrow 0$ because the potential is now weak relative to the particle energy. Of course $\sigma(K \rightarrow \infty)$ decreases even more quickly because of the K^{-2} term.

14.5 Partial Waves in the Classical Limit - Hard Spheres

Consider the scattering of a small hard sphere (radius x_m , mass m) by a large hard sphere (X_M , M). Firstly we transform the problem to the centre of mass reference frame where it becomes that of a single effective particle of mass $\mu = mM/(m + M)$ moving in a hard sphere potential ($V(r < r_H = X_M + x_m) = \infty$). Thus the boundary condition is $R_l(r_H) = 0$.

Consider the classical limit, where the sphere radius is much larger than the de Broglie wavelength, $kr_H \gg 1$. Up to $l = Kr_H$ the phase shift is enormous and $\sin \delta_l$ could have any value. For $l > Kr_H$ the impact parameter is so large that the particles miss and $\delta_l = 0$. Thus we can write the scattering cross section:

$$\sigma = \frac{4\pi}{K^2} \sum_{l=0}^{l=Kr_H} (2l+1) \frac{1}{2}$$

where we replace $\sin^2 \delta_l$ with its average value of $\frac{1}{2}$.

Since Kr_H is large, we can replace the sum by an integral and take only the leading term; $(Kr_H)^2 \gg Kr_H$:

$$\sigma \approx \frac{2\pi}{K^2} \int_{l=0}^{l=Kr_H} (2l+1) dl \approx 2\pi r_H^2$$

This result should send us rushing back to look for the extra factor of 2, since the cross-section of a sphere might be expected to be πr_H^2 . In fact, though, the analysis is correct and closer analysis of the θ dependence of the wavefunction shows that half the amplitude is diffracted into the classical 'shadow' of the sphere to cancel the amplitude of the unscattered wave there.

14.6 Ramsauer-Townsend effect

This is the name given to the fact that electrons with energy about 1eV can pass almost freely through Xe, Kr, and Ar:- there is a sharp minimum in electron scattering cross-section for these noble gases.

Due to polarisation of these atoms by the incoming electron the potential appears to increase as K increases (more localised electrons are better able to polarise the atom). Thus $\delta_0(k \rightarrow 0) = n\pi$, in accordance with Levinson's theorem, and δ_0 initially increases as k increases, before eventually decreasing. Thus at a certain value of k , the phase shift is again $\delta_0(k) = n\pi$, and the total scattering cross section σ_T has an abrupt minimum. Although there are subsequent s -wave minima at e.g. $\delta_0(k) = (n-1)\pi$, these occur at sufficiently large values of k that s -wave scattering is no longer dominant.

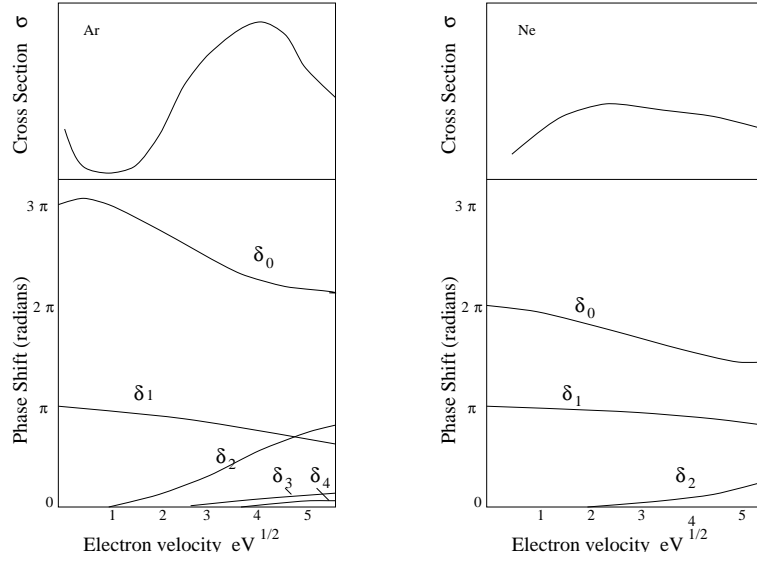


Figure 15: Minimum in scattering cross section in Ar due to $\delta_0 = 3\pi$; No such effect in Ne due to weaker polarisation.

By contrast, neon and helium have lower polarisability, due to fewer bound electrons. Thus the phase shift δ_0 decreases monotonically with k from $n\pi$ at $k = 0$ at there is no low-energy minimum. Higher l phase shifts may increase with k because higher k implies smaller impact parameter (classically, more chance of hitting the atom). The cross section increases more slowly due to the additional K^{-2} dependence. The maximum in the Ar cross section at about 13eV is mainly due to the d -wave $\delta_2 = \pi/2$.

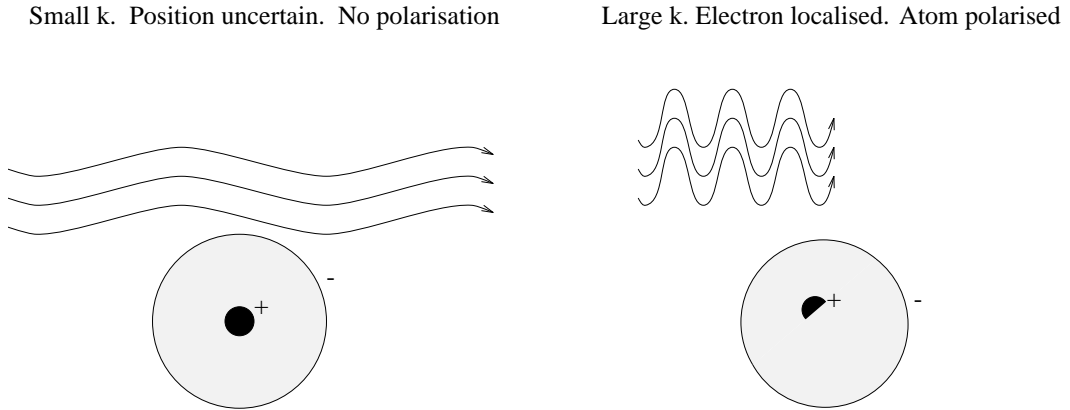


Figure 16: More-localised electrons polarise atoms and thus increase the attractive potential

15 Bits and pieces

15.1 Casimir effect - forces from nothing

For many quantum systems, such as the harmonic oscillator, there is still some energy associated with the lowest quantum state. This “zero-point” energy is real, and can be measured in the ‘Casimir effect’. There is a force between two metallic plates in a vacuum, because moving them would change the wavelength/energy of the zero-point quantised electromagnetic waves between them: this change in energy in response to a move equates to a force.

The wavefunction for transverse standing electromagnetic waves between plates of area A separated by a in the z -direction is:

$$\Phi_n = \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega_n t)] \sin(k_n z)$$

where \mathbf{k} lies in the xy plane and $k_n = n\pi/a$. The energy is $E_n = \hbar\omega_n = hc/\lambda = \hbar c \sqrt{\mathbf{k}^2 + k_n^2}$

$$\text{and the force per unit area is } F = -\frac{dE}{da} = \frac{d}{da} \left(\hbar \int \sum_{n=1}^{\infty} \omega_n \right) dk_x dk_y / (2\pi)^2 = -\frac{\hbar c \pi^2}{240 a^4}$$

Solving this involves a trick of multiplying each term by $|\omega_n|^{-s}$, then taking the limit of $s = 0$. This tiny attractive force has now been measured (Bressi, Phys.Rev Letters, 2002)

15.2 What does it mean: Wavefunction collapse and the EPR paradox

The interpretation of collapsing wavefunctions is often regarded as unphysical, or philosophically problematic. There appears to be a contradiction with relativity in the idea that the wavefunction collapses instantaneously throughout space, although the wavefunction is not measurable.

An attractive contrary view to the idea of ‘measurement collapsing the wavefunction’ is that for a particular system the value of an observable is a property of the particle, and the wavefunction only expresses averages over many particles. This kind of property is known as a hidden variable. As we shall see, this interpretation of quantum mechanics can be tested, and is inconsistent with experimental results.

Consider a two-photon decay from a source (e.g. ^{40}Ca). Two polarisers are oriented along the z -direction, and we detect whether or not the photons pass through the polariser.

The decay is one in which angular momentum is conserved, so the photons must be either both right-polarised (\mathbf{e}_R) or both left-polarised (\mathbf{e}_L) (they travel in opposite directions). We are dealing with bosons, so the wavefunction can be written as a superposition:

$$|12\rangle = \sqrt{\frac{1}{2}} (\mathbf{e}_{1R}\mathbf{e}_{2R} + \mathbf{e}_{1L}\mathbf{e}_{2L})$$

Now convert into x and y polarisation using $\mathbf{e}_R = (\mathbf{e}_x - i\mathbf{e}_y)$ and $\mathbf{e}_L = (\mathbf{e}_x + i\mathbf{e}_y)$ to give

$$|12\rangle = \sqrt{\frac{1}{2}} (\mathbf{e}_{1x}\mathbf{e}_{2x} + \mathbf{e}_{1y}\mathbf{e}_{2y})$$

From this we can clearly see that the quantum probability of the photon 1 passing through its detector is $\frac{1}{2}$, and if so the wavefunction collapses onto $|12\rangle = \mathbf{e}_{1x}\mathbf{e}_{2x}$ and the conditional probability of the second photon passing through its detector is then 1. Thus quantum mechanics tells us that the probability of both detectors counting is $\frac{1}{2}$.

Contrariwise, a hidden variables argument might say that on production the photons were polarised in a random direction, say θ to the x -axis. In this case the probability of passing through

either detector would be $\cos^2 \theta$, and the probability of simultaneous counts will be $\langle \cos^4 \theta \rangle = 3/8$. The mathematics for particles with correlated spins is similar.

Since the wavefunction collapse and hidden variable approach give different answers, we can do an experiment to see which is correct.

15.3 Hidden Variables: Bell's Inequality and Aspect's experiment

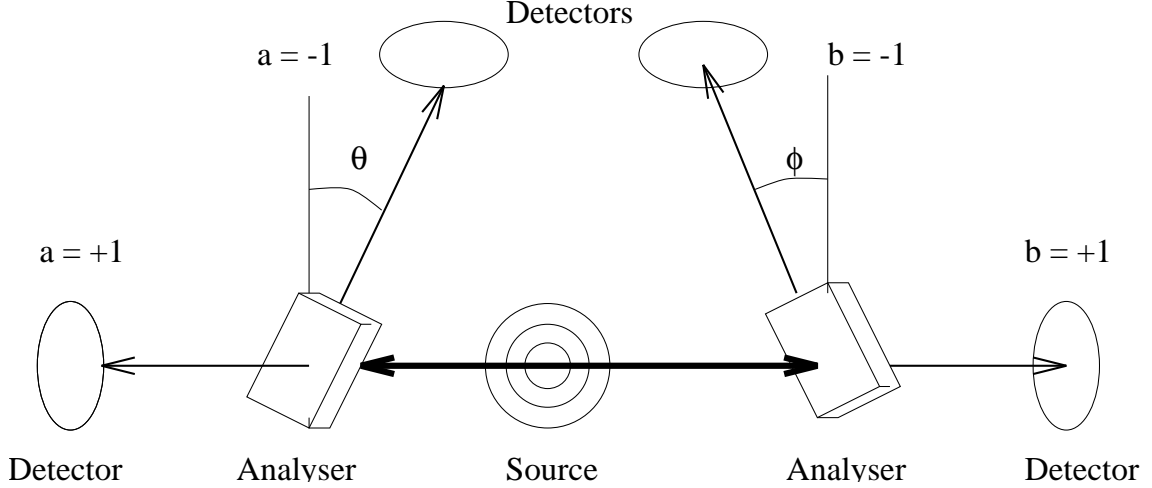


Figure 17: Aspect's Experiment: The polarisations of both photons from the two-photon ^{40}Ca source are measured by analysers at angles of θ and ϕ .

Consider extending the experiment described above to the case of analysers at arbitrary angles which detect all photons. We define measurables $a(\theta)$ and $b(\phi)$ as +1 if the photon is aligned with the analyser and -1 if it is opposed. What, then, is the ensemble average value of $P(\theta, \phi) = \langle a(\theta)b(\phi) \rangle$? Clearly, if $a(\theta)$ and $b(\phi)$ are uncorrelated $P=0$, but since they come from a common source, this is not the case: their wavefunctions are sometimes referred to as 'entangled'.

If the photons start out with 'hidden variable' polarisation χ , then it is easily shown that:

$$P_{HV}(\theta, \phi) = \frac{1}{2\pi} \oint \left(\cos^2(\theta - \chi) - \sin^2(\theta - \chi) \right) \left(\cos^2(\phi - \chi) - \sin^2(\phi - \chi) \right) d\chi = \frac{1}{2} \cos 2(\theta - \phi)$$

Meanwhile if the wavefunction collapses at the first measurement, taken arbitrarily as A:

$$P_{QM}(\theta, \phi) = \frac{1}{2\pi} \oint \left(\cos^2(\theta - \chi) - \sin^2(\theta - \chi) \right) \left(\cos^2(\theta - \phi) - \sin^2(\theta - \phi) \right) d\chi = \cos 2(\theta - \phi)$$

In 1982, to test this Aspect carried out measurements on ^{40}Ca decays using two different angles for both θ and ϕ . The quantity he evaluated was:

$$S(\theta_1, \phi_1, \theta_2, \phi_2) = P(\theta_1, \phi_1) + P(\theta_2, \phi_2) + P(\theta_2, \phi_1) - P(\theta_1, \phi_2)$$

Where he chose the values which give the largest S: $\theta_1 = \phi_1 + \frac{\pi}{8} = \theta_2 + \frac{2\pi}{8} = \phi_2 + \frac{3\pi}{8}$

The hidden variables theory suggests the result should be $S=\sqrt{2}$, while the wavefunction collapse suggests $S=2\sqrt{2}$ with perfect measurement devices. Imperfections in the measurement will reduce the measured correlation in each case. Aspect measured $S = 2.697 \pm 0.015$, confirming the quantum prediction.

The apparent complexity of Aspect's experiment is needed to eliminate sources of error due to detector, analyser and source imperfections.

There is an apparent contradiction between quantum mechanics and relativity, in that the *interpretation* of quantum mechanics requires *instantaneous* collapse of the wavefunction. There is no *measurable* quantity for which the two theories give different predictions. "Teleportation" can transport a quantum state arbitrary distances, but it doesn't transfer information instantaneously.

Most of the wavefunctions we have solved are from Schrodinger's equation, which treats time and space in different ways. For a properly relativistic approach, they should be equivalent. This discrepancy between quantum and relativity is easily resolved: the Dirac equation provides a fully relativistic wave equation for which the Schrodinger equation is a low energy approximation. A nice thing about the Dirac equation is it can only be solved by spinors: as with quantisation the observed physics turns out to be the only way to solve the mathematics.

The three original papers described in this section are beautifully clear, copies are linked from the course webpage.

15.4 When can things interfere? What counts as a measurement?

Interference from two slits of a single particle with itself remains a difficult concept to understand.

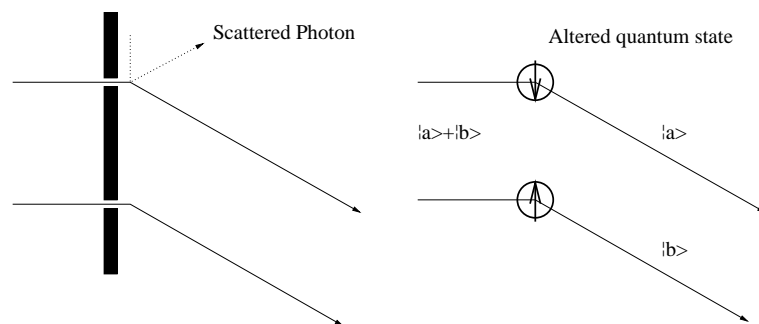


Figure 18: Feynman's 'classical' explanation of the destruction of the interference pattern by measurement, and two separate demonstrations that it is really a quantum effect

Feynman introduced a nice argument based on the uncertainty principle. He argued that the wavelength of light required to detect which way a particle went must be smaller than the slit separation. From the uncertainty principle, it follows that the momentum transfer must be so large that it would destroy the interference pattern. Thus the measurement device destroyed the interference. Unfortunately, more recent experiments show things are more complicated than that.

Eichmann *et al* (Phys.Rev.Lett, 1993) set up a 'two slit' experiment using photon with lead atoms as the scatterers. With careful choice of energy, he was able to arrange that the scattering event changed the internal electronic state of the atom: a process which requires negligible momentum transfer but would allow subsequent measurement of the atomic state and determination which way the particle went. As a consequence, the interference fringes vanish.

Durr *et al* (Nature, 1998) used a standing light wave to scatter rubidium atoms. Added to this was a microwave source which changed the hyperfine state of the atoms at one of the "slits", which could in principle be measured but supplies negligible momentum. The interference pattern disappeared.

Again, quantum mechanics has been shown to give a correct description: non-identical wavefunctions do not interfere even if they describe the same particle! It does not matter whether the measurement of the internal states is actually performed: the mere fact that it could be is enough to destroy the interference.

15.5 Relativistic Quantum Mechanics

The Schrodinger equation itself is clearly inconsistent with relativity; It has second derivatives of space, and first derivatives of time. If we use the relativistic expression for energy $E^2 = |\mathbf{p}|^2 c^2 + m^2 c^4$ we obtain

$$-\hbar^2 \frac{\partial^2}{\partial t^2} \phi(\mathbf{r}, t) = -\hbar^2 c^2 \nabla^2 \phi(\mathbf{r}, t) + m^2 c^4 \phi(\mathbf{r}, t)$$

which is called the Klein Gordon equation. It has solutions describing a relativistic quantum particle, but others which describe particles of negative total energy, together with negative probabilities for finding them! Applied to hydrogen it gets the relativistic kinetic energy correction correct, but it doesn't account for other observed relativistic effects, such as the spin-orbit correction or the Darwin term (see Atomic and molecular physics).

Dirac tried keeping time and space on an equal footing using a linear equation

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \{c \underline{\alpha} \cdot \underline{\hat{p}} + \beta mc^2\} \psi(\mathbf{r}, t) = \hat{H} \psi(\mathbf{r}, t) \quad \text{where} \quad \underline{\alpha} \cdot \underline{\hat{p}} = -i\hbar \left(\alpha_x \frac{\partial}{\partial x} + \alpha_y \frac{\partial}{\partial y} + \alpha_z \frac{\partial}{\partial z} \right)$$

Consider a *free particle*, no terms in the Hamiltonian \hat{H} should depend on \mathbf{r} or t as these would describe forces. Dirac assumed that α_i and β are independent of position, time, momentum and energy, so $\underline{\alpha}$ and β commute with \mathbf{r} , t , $\underline{\hat{p}}$ and E but not necessarily with each other.

Since relativistic invariance must be maintained, *ie* $E^2 = |\underline{p}|^2 c^2 + m^2 c^4$,

$$\begin{aligned} \hat{H}^2 \psi(\mathbf{r}, t) &= (c^2 |\underline{\hat{p}}|^2 + m^2 c^4) \psi(\mathbf{r}, t) \\ &= \{c \underline{\alpha} \cdot \underline{\hat{p}} + \beta mc^2\} \{c \underline{\alpha} \cdot \underline{\hat{p}} + \beta mc^2\} \psi(\mathbf{r}, t) \end{aligned}$$

Expand the RHS of this equation, being very careful about the ordering of α_i and β

$$\begin{aligned} \hat{H}^2 \Psi(\mathbf{r}, t) &= \left\{ c^2 [(\alpha_x)^2 (\hat{p}_x)^2 + (\alpha_y)^2 (\hat{p}_y)^2 + (\alpha_z)^2 (\hat{p}_z)^2] + m^2 c^4 \beta^2 \right\} \psi(\mathbf{r}, t) \\ &\quad + c^2 \left\{ (\alpha_x \alpha_y + \alpha_y \alpha_x) \hat{p}_x \hat{p}_y + (\alpha_y \alpha_z + \alpha_z \alpha_y) \hat{p}_y \hat{p}_z + (\alpha_z \alpha_x + \alpha_x \alpha_z) \hat{p}_x \hat{p}_z \right\} \psi(\mathbf{r}, t) \\ &\quad + mc^3 \left\{ (\alpha_x \beta + \beta \alpha_x) \hat{p}_z + (\alpha_y \beta + \beta \alpha_y) \hat{p}_z + (\alpha_z \beta + \beta \alpha_z) \hat{p}_z \right\} \psi(\mathbf{r}, t) \end{aligned}$$

relativistic invariance for the free particle requires that the second and third term are zero, and so

$$\begin{aligned} (\alpha_x)^2 &= (\alpha_y)^2 = (\alpha_z)^2 = \beta^2 = 1 \\ \alpha_i \alpha_j + \alpha_j \alpha_i &= 0 \quad (i \neq j) \\ \alpha_x \beta + \beta \alpha_x &= 0 \quad (\text{and similarly for } y, z) \end{aligned}$$

Thus α_i and β cannot be just numbers. The simplest representation for α and β are 4x4 matrices, meaning that the wavevector is a 4-component vector. When we work this through, there are no negative probabilities, but two of the components turn out to have negative energy. Full details of the derivation are on the course website.

It turns out that the four components accurately describe the two spin states of the electron and the positron. More remarkably, Dirac solved the equation before the positron had even been discovered!